UTILIZATION OF HOUSEHOLD ORGANIC WASTE AS POTENTIAL ADSORBENT FOR HEAVY METALS REMOVAL FROM SYNTHETIC AQUEOUS SOLUTIONS

BY

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This thesis, written by **Abdullah Abdulkarem Basaleh** under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

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This work is dedicated to my family and friends

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AC : Activated Carbon

BET : Brunauer Emmett Teller

Ce : adsorbate concentration at equilibrium (mg/L)

Ci : adsorbate initial concentration (mg/L)

EDX : Energy Dispersive X-ray

FTIR : Fourier Transform Infrared

HOW : Household Organic Waste

K_1 : Pseudo-first-order constant rate (1/min)

K_2 :Pseudo-second order rate constant (g/mg min)

K_F : Freundlich constant

1/n : Heterogeneity factor of Freundlich

q_e : equilibrium adsorption capacity (mg/g)

q_t :Adsorption capacity at time t (mg/g)

TGA : Thermo-Gravimetric Analysis

WHO : World Health Organization

XRD : X-Ray Diffraction spectroscopy

ABSTRACT

Full Name : Abdullah Abdulkarem Basaleh

Thesis Title : Utilization of Household Organic Waste as Potential Adsorbent for Heavy Metals Removal from synthetic Aqueous Solutions

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Due to large industrial activities, including electroplating, electrical, batteries, and pesticides, large quantities of heavy metals are being discharged into wastewater in daily basis, which cause seriously hazardous environmental problems. Among various techniques for heavy metals removal from wastewater, adsorption is considered as one of the best widely used techniques in wastewater treatment due to its simplicity and efficiency. Activated carbon is one of the most extensively adsorbents used for heavy metals removal through adsorption process due its large surface area.However, commercial activated carbon is expensive, so recently, numerous studies have been conducted in the utilization of waste materials as low cost precursor of activated carbon. Household organic waste is abundant and rich in carbon, so, in this study, it was utilized as potential low cost source of activated carbon. Activated carbon was prepared through chemical activation process using two activating agents, namely potassium hydroxide and phosphoric acid. The precursor was carbonized at different temperatures. The produced activated carbon was characterized by the standard methods. At the best activation conditions, highest surface area obtained was around 790 m^2/g. The produced AC was

tested for its performance in heavy metals removal from synthetic industrial wastewater through adsorption experiments. The adsorption experiments were conducted in the batch mode and concentrated on the adsorption of Cadmium (Cd) and Lead (Pb) ions from synthetic solutions in single as well as binary systems. The effect of operational parameters such as contact time, pH, and adsorbent dosage on the adsorption behavior was also investigated. The experimental data of adsorption was fitted to Langmuir and Freundlich, where good fitting was observed. In addition, pseudo-first order and pseudo-first order kinetic models were fitted to the experimental data.

Key words: Household organic waste; Activated carbon; Adsorption; Heavy metals removal.

ملخص الرسالة

الاسم الكامل: عبدالله عبدالكريم عبود باصالح

عنوان الرسالة: دراسة امكانية الاستفادة من المخلفات العضويه للمنازل في معالجة المياه الملوثة بالمعادن الثقيلة

التخصص: هندسة مدنية

تاريخ الدرجة العلمية: مايو, 2015

نتيجة للتوسع الكبير في النشاط الصناعي في مختلف المجالات , مثل صناعة البطاريات, الطلاء والمبيدات الحشرية, فان كميات كبيرة من المعادن الثقيلة يتم تصريهفها بشكل يومي في مياه الصرف .وجود هذه المعادن الثقيلة يسبب مشاكل صحية وبيئية بالغة الخطورة. من بين الطرق المتاحة لمعالجة المياه الملوثة بالمعادن الثقيلة طريقة الامتصاص والتي تعتبر من افضل الطرق المستخدمة نظرا لسهولتها وكفاءتها. الكربون المنشط يعتبر من افضل المواد المستخدمة في ازالة المعادن الثقيلة عن طريق الامتصاص نظرا لمساحته السطحية الكبيرة, ولكن السعر المرتفع للكربون المنشط جعل استخدامه محدود نسبيا , لذلك في السنوات الاخيرة تم استغلال النفايات بمختلف انواعها في انتاج الكربون المنشط بغرض التقليل من كلفة الانتاج المرتفعة و قد اجريت عدد كبير من الدراسات في هذا المجال. مخلفات المنازل العضوية (بقايا الاطعمة) وفيرة وغنية بالكربون , لذلك تم في هذا البحث دراسة امكانية استخدامها كمصدر منخفض التكلفة في انتاج الكربون المنشط, والذي بدوره ايضا سيمثل طريقة مثالية في التخلص من هذه النفايات بطريقة فعالة . تم انتاج الكربون المنشط عن طريق التنشيط الكيميائي , حيث استخدم هيروكسيد البوتاسيوم بالاضافة الى حمض الفسفوريك في عملية التنشيط. الكربون الذي تم تحضيره باستخدام حمض الفوسفوريك اعطى نتائج افضل من حيث الكمية الناتجة بعد الحرق والمساحة السطحية. تم حرق النفايات المنزلية عند درجات حرارة مختلفة ومن ثم تم اختبار الكربون الناتج بطرق الاختبار القياسية . من خلال النتائج تبين ان افضل الظروف لانتاج الكربون باستخدام حمض الفوسفوريك هي : درجة حرارة 700 درجة مئوية, الزمن ساعتين , تركيز الحمض هو 30 %. حيث ان المساحة السطحية الناتجة هي 793 م^2/جم . تم استخدام هذه العينة في ازالة العناصر الثقية من خلال عملية الامتصاص. تم في هذا البحث التركيز على ازالة العناصر التالية : الرصاص و الكادميوم .تم دراسة تأثير بعض المتغيرات التشغيلية مثل وقت الاتصال بين الكربون المنشط والمحلول بالاضافة الى كمية الكربون المنشط المستخدمة في عملية الامتصاص. النتائج التي تم الحصول عليها من عملية الامتصاص درست من حيث تطابقها مع نموذج (انجميور) و (فروندليتش) حيث لوحظ تطابق جيد مع النموذجين .

CHAPTER 1

INTRODUCTION

Due to large industrial activities such as electroplating, mining, car manufacturing, electrical, batteries, and pesticides, large quantities of heavy metals are being discharged into wastewater in daily basis [1]. Beside the toxicity of heavy metals, they are non-biodegradable and accumulate in food chain and in human tissue, causing many serious health and environmental problems[2,3]. Consequently, it is necessary to control the concentrations of these metals in wastewater in order to satisfy the limits of standard regulations and avoid the associated problems.

In light of the above, many technologies have been used to treat heavy metals polluted wastewater such as ion exchange, electrochemical treatment, adsorption, and reverse osmosis. However, some of them are either expensive or possess several limitations. The advantages and drawbacks of every method have been widely discussed by Barakat [4]. Due to its simplicity in design and operation; and applicability for the removal of numerous pollutants, adsorption is one of the best widely used techniques in wastewater treatment [5]. Activated carbon is one of the most extensively adsorbents used for heavy metals removal through the adsorption process. However, sometimes it is limited due to high production cost of the commercial activated charcoal. As a consequent, large numbers of researches have been conducted to investigate low cost alternative adsorbents such as waste of different agricultural crops [6]. Most of the

studied biosorbents were investigated individually; very few studies investigate the adsorption behavior of mixed species, such as household organic waste.

Domestic organic waste including household waste is expanding significantly every year. Tremendous amounts of solid waste are annually produced in Saudi Arabia. About 12 million tons of total domestic solid waste is annually generated in the Kingdom, where organic waste represents about 79% [7]. This huge amount of waste usually comes from household, restaurants, hotels, industrial, construction and agricultural waste. Household waste usually consists of several waste materials such as papers, wood, organic and vegetables, plastic, metals, glass, and textiles. However, the organic and vegetable waste materials represent the highest portion, especially in Saudi Arabia as shown in Table 1.1 [8].

Table 1.1: Domestic waste composition in Middle Eastern countries [8]

Type of waste	Percentage by weight						
	Kuwait	N.Yemen	U.A.E		Saudi Arabia		
	Safwa	Sanaa	Dubai	Al-Ain	Dammam	Khobar	Jeddah
Fine dust and cinders under 10 mm	-	18	2	4			
Organic and vegetable	30	56	41	21	61	57	52
Paper, board, and wood	40	6	41	39	15	17	19
Metals	5	8	7	15	7	7	10
Textiles	2	1	4	3	5	7	2
Glass	2	2	3	5	5	7	7
Plastic	6	1	2	5	7	10	20
Unclassified	15	8		8	5	2	

Household organic and vegetable waste are abundant and rich in carbon. Consequently, it could be utilized as promising low cost source of activated carbon. Despite the fact that numerous of household organic waste is utilized as food for livestock or garden fertilizer, a great part just dumbed in land fill sites [9], so two major advantages would be achieved when using household organic waste as biosorbent; low cost production of activated carbon and effective environmental friendly waste disposal.

1.1 Objectives

Based on the comprehensive literature review, great number of studies in the utilization of waste materials as promising low-cost adsorbent for heavy metals removal from aqueous solutions have been conducted. However, very few studies investigate the adsorption behavior of mixed species, such as household organic waste, it is clear that there is a lack of information in this field in the Kingdom of Saudi Arabia. Accordingly, the primary objective of this study is to investigate the potentiality of utilizing household organic waste produced in the Kingdom of Saudi Arabia as inexpensive adsorbents for the removal of heavy metals produced from various industrial activities. For this purpose, the study will concentrate on well-mixed household organic waste consisting of varying amount of several components of food residues, including peels of orange, banana, lemon, and potato as well as melon and watermelon shell, onion skin and stalk, egg shell, bread crumbs, bone of fish and animals, and others. The specific objectives of this research are:

1. Investigate the production of activated carbon through chemical activation from well-mixed household organic waste using several activation conditions with two activating agents; H_3PO_4 and KOH.

2. Investigate the potentiality of utilizing household organic waste based activated carbon, for the removal of Cd (II) and Pb (II) from synthetic industrial wastewater.

3. Study the effect of different parameters of adsorption process including pH, Contact time, initial concentration, and adsorbent dosage.

4. Investigate the effect competitive adsorption.

5. Investigate the equilibrium adsorption isotherm model that will best fit the obtained results.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater treatment

Water pollution is increasingly in the rise due to rapid urbanization and industrial development, so providing renewable water is utmost priority. Many wastewater treatment technologies have been introduced with varying degrees of success including filtration, evaporation, reverse osmosis, coagulation, activated sludge, foam flotation , microbial reduction, ion exchange, aerobic and anaerobic treatment, electrolysis, solvent extraction, advanced oxidation process and adsorption [10]. According to Bhatnagar & Sillanpää [10], the appropriate technology will depend on a number of factors, namely waste disposal constrain, required degree of purification, cost, the size of the treatment facility and reliability of process equipment. The advantages and drawbacks of every method have been widely discussed by Barakat [4].

2.2 Adsorption

Definition

"Adsorption is the process by which the ions or molecules present in one phase tend to condense or concentrate on the surface of another phase." Adsorption process is divided to three types; chemical, physical and exchange adsorption. The material being adsorbed is called adsorbate, whereas the adsorbing material is called adsorbent [11].

Adsorption process is considered one of the best available wastewater treatment techniques, which can be attributed to its simple design and operation, as well as its ability to remove different types of pollutants [12]. Consequently, adsorption process has been applied in wide range for the removal of solutes from aqueous solution.

The adsorption concept was first presented by Gibbs [13], whereas the first quantitative studies started in 1773 by C.W. Scheele [14], and ever since then, the adsorption process has been widely employed in the field of wastewater treatment. An extensive revision regarding the theory and application of adsorption is made by Dabrowski [13].

2.3 Adsorption Isotherms

The quantitative relationship between the adsorbate concentration (mass/volume) in solution and its adsorbed concentration (mass adsorbate/mass adsorbent) at the equilibrium at constant pH and temperature is called adsorption isotherms [7,11], which are considered as the main source of information on the adsorption process [13]. Complex analytical formulas can be used to characterize the adsorption isotherms that assume heterogonous characteristic for adsorbents which is valid for activated carbons. The analytical models either empirical, which fit experimental data in equations, or depends on simplified physical adsorption picture [16]. The most commonly used mathematical models are Linear, Langmuir, Freundlich and BET (Brunauer, Emmett, and Teller). The linear isotherm is considered as special case of the Freundlich isotherm [11].

2.3.1 Langmuir Isotherm

The Langmuir isotherm is an empirical model. Its formula is the first equation theoretically presented [17], which was basically developed to characterize gas-solid-phase adsorption [15]. This isotherm assumes monolayer adsorption, which means that once the molecule of the adsorbate connects to the adsorbent surface, no more adsorption occurs. In addition, it assumes that affinity for the adsorbate in all surface sites of the adsorbent is equal [11]. According to Bansal and Goyal [17], Langmuir isotherm neglects the lateral interaction between the adsorbed entities and assumes homogenous and completely smooth surface.

The Langmuir isotherm formula is expressed as following:

$$q = q_m \frac{K_{ads} C}{1 + K_{ads} C}$$

Where q is adsorption density (mass adsorbate /mass adsorbent), q_m is maximum capacity of adsorbent, C is aqueous concentration of adsorbate (mass/volume), K_{ads} is affinity measure of adsorbate for adsorbent.

The linear form of Langmuir isotherm shown below can be used to calculate K_{ads} and q_m by plotting 1/q versus 1/C [11].

$$\frac{1}{q} = \frac{1}{q_m K_{ads}} \left(\frac{1}{C}\right) + \frac{1}{q_m}$$

2.3.2 BET Isotherm

According to Dabrowski [13], although the BET theory has a number of restrictions, it was the first effort that made universal theory of physical adsorption. BET

isotherm was developed by Brunauer, Emmett, and Teller. It is extensively used in gas-solid equilibrium system [18]. BET isotherm was extended from Langmuir isotherm by assuming multi adsorption layers, and that each layer follows Langmuir isotherm [11]. The first layer of adsorbate is strongly connected to the adsorbent surface whereas the second layer is adsorbed by the first layer and so on until number of layers are build up [16].

The BET isotherm equation is shown below

$$\frac{q}{q_m} = \frac{bC}{(C_s - C)[1 + \frac{(b-1)C}{C_s}]}$$

Where C_s is the adsorbate saturation concentration in the solution, q is adsorption density (mass adsorbate /mass adsorbent), q_m is maximum capacity of adsorbent, and C is aqueous concentration of adsorbate (mass/volume). The linear form of BET isotherm shown below can be used to calculate C_s and b by plotting $C/q(C_s-C)$ versus C/C_s .

2.3.3 Freundlich Isotherm

Freundlich isotherm is the first isotherm that was used to describe the relationship of non-ideal and reversible adsorption [15]. The affinity in Freundlich isotherm is non-uniform over the surface of the adsorbent and each site on the adsorbent surface has different affinity. Consequently, the site that has stronger affinity for the adsorbate is occupied first [11]. This isotherm assumes multilayer adsorption, where maximum adsorption capacity occurs at the beginning and then it decreases exponentially until the end of the adsorption process [18]. Freundlich equation takes the following formula

$$q = K\, C^{1/n}$$

Where K is adsorbent capacity measure (mass adsorbate/ mass adsorbent), n is measure of affinity change for the adsorbate due to change in adsorption density, if n = 1, it means that all sites on the adsorbent surface have the same affinity and the isotherm become linear. If n > 1, this means that as the adsorption density increases the affinities decrease. The linearized form of Freundlich isotherm shown below can be used to evaluate K and n by plotting log q versus log C [11].

$$\log q = \log K + \frac{1}{n} \log C$$

2.4 Activated Carbon

Many materials have been used as adsorbent in wastewater treatment such as silica gels, activated alumina, zeolites, and activated carbon [10]. Among these materials, the activated carbon is the most popular and extensively used adsorbent for many applications. This can be attributed to many features of activated carbon, namely, high surface area which ranges from 500 to 1500 (m^2/g) [17], (but it could reach in excess 3000 (m^2/g)), high degree of surface reactivity, and variable characteristics of surface chemistry [19].

Approximately 80% of activated carbon all over the world is used in the application of liquid phase. [20]. Recently, great number of researchers used activated carbon to remove several pollutants, including metals [21], phenols and dyes [22], herbicides [23], Organics [24] , and many other chemicals.

2.5 Activated carbon preparation

Method of preparation as well as carbon precursor play key role in microporosity of produced activated carbon [25]. The preparation of activated carbon basically consists of two major processes; carbonization of raw material and activation. Carbonization is the process by which non carbon elements are removed from raw material whereas carbon content is increased at high temperatures which usually vary between 400 and 800 ^{o}C [26]. Temperature should be selected carefully because it is the major factor that the desired product of carbonization basically depends on [17].

2.5.1 Activation process

Generally, the activation process occurs after carbonization process. The main purpose of activation is to inhance the internal surface area and develop the porosity, which in turn, increases the sorption capacity of carbonized material [27].

2.5.1.1 Physical activation

In physical activation process, reaction occurs between carbon and oxidizing gas such as oxygen, carbon dioxide or carbon monoxide, in the presence of high temperature. This reaction results in opening the pore that where closed by removing the blocking substances [17].

2.5.1.2 Chemical activation

Usually in the chemical activation, carbonization and activation occurs altogether in one step. However, some times, they can be done separately [17]. In this process, the carbon reacts with chemical activating agent, including $ZnCl_2$, KOH, H_3PO_4, and K_2CO_3

at high temperatures, where oxygen and hydrogen are removed from carbon structure. This reaction results in higher surface area at lower temperature and less duration compared to physical activation. On the other hand, it has some disadvantages such as cost of activating agents and washing processes to remove them. It was reported that the highest obtained surface area is 3000(m^2/g), when KOH was used as activating agent [19].

2.6 Activated carbon classification

Activated carbon can be classified into many different classifications based on preparation method, surface properties, or physical characteristics, but based on the particle size, it can be classified generally to three groups; Powder, Granular, and Fiber activated carbon.

2.6.1 Powder Activated Carbon (PAC)

According to the American Water Works Association Standard (AWWA), the powder activated carbon is defined as crushed carbon particles which 95%-100% of it will pass through sieve No. 50 (0.297 mm), or sieve No. 80 (0.177 mm) according to the ASTM. It is widely used in the treatment of waste and potable water [28].

2.7 Heavy metals removal

Heavy metals are regarded as one of the most toxic pollutants in wastewater. They are usually produced from several industrial activities such as manufacturing different products, metal plating and mining, as well as the agricultural activities where fertilizers are used [19]. Several heavy metals were considered by World Health Organization

(WHO) as the most toxic pollutants ; chromium, mercury, copper, cadmium nickel and lead [29]. In addition to the toxicity of heavy metals, they are non-biodegradable and accumulate in food chain and under human tissue, causing many hazardous health problems, so its concentration must not exceed the standard limits. Table 2 summarize the health problems and the maximum allowable concentrations levels (MCL) in drinking water according to the United States Environment Protection Agency (USEPA) [3].

Table 2.1: The maximum Concentration limit (MCL) and the hazardous health problems of heavy metals

Heavy Metal	Toxicities	MCL(mg/L)
Arsenic (As)	Skin manifestations, visceral cancers, vascular disease	0.05
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen	0.01
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper (Cu)	Liver damage, Wilson disease, insomnia	0.25
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.2
Zinc (Zn)	Depression, lethargy, neurological signs and increased thirst	0.8
Lead (Pb)	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury (Hg)	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Activated carbon is widely used for the removal of heavy metals efficiently and economically acceptable [30]. Activated carbon from inexpensive sources such as waste materials will be promising substitute for the removal of heavy metals. From this

perspective, large numbers of researches have been conducted in the utilization of waste materials as an inexpensive potential adsorbent source.

2.7.1 Cadmium and lead Toxicity

Cadmium is silver-white heavy metal, it has atomic number of 48, atomic mass of 112.4 g/mole, electronegativity of 1.7, ionic radius of 0.097 nm. [1]. Cadmium could primarily be present in the earth crust. It is usually found in conjunction with zinc. The main source of cadmium is industrial waste water including steel plating, plastics and batteries. It is also can be produced as emission from artificial fertilizer [2]. After getting utilized, it gets into the environment primarily through the ground, since it can be found in manures in addition to pesticides.

It is considered by the WHO as the second most toxic metal after mercury since the MCL of it is the lowest after mercury, as illustrated in table. The exposure to high concentration of cadmium can cause many serious health problems such as kidney damage, other associated problems are shown in the table 2.10. Moreover, it is well known that the high concentration can cause itai-itai disease [3]

Lead is bluish-white heavy metal, it has atomic number of 82, atomic mass of 207.2 g/mole, electronegativity of 2.33, ionic radius of 0.132 nm and density of 11.34 g/cm^3. [1].Lead usually be present in ore with copper, zinc, and silver. it gets into the environment from industrial activities such as batteries, petrochemicals, and explosive manufacturing, or through car exhausts [4]. It is also get to the human body from water, food, and air. , since it can be produced from corrosion of pipes. [1]

It is considered by the WHO as the third most toxic metal after mercury and lead since the MCL of it is the lowest after these to heavy metals, as illustrated in table. The exposure to high concentration of lead can cause many serious health problems such as brain damage, other associated problems are shown in the table 2.10.

2.8 Household organic waste

Household organic waste can be utilized in producing activated carbon, which in turn, used in wastewater treatment through adsorption process. The carbon produced from waste materials has two major advantages; low cost production and effective waste disposal. Waste materials are abundant, inexpensive and have considerable amount of organic content. Consequently, they can be used effectively as potential inexpensive adsorbents [20]. The household organic waste is normally made of food residue such as fruit and vegetable waste, some bread crumbs, egg shells, bone fragment of animals and fishes, and many others, so organic waste materials can be divided based on the origin into agricultural, and non-agricultural waste materials. Large numbers of researches have been conducted in the utilization of waste material as low-cost adsorbent in the last decades. Some relevant waste materials that have been studied as potential adsorbents for heavy metals removal are presented in Table 3 and 4.

2.8.1 Agricultural household waste materials

Agricultural waste materials is very important source of carbon due to its high content of cellulose [31]. They are abundant and obtained almost for free, which encouraged many researchers to investigate them as potential low-cost adsorbents. Recently, large number of agricultural waste materials have been studied as potential low cost adsorbents, including rice, wheat, tea, coffee, coconut, peanut, orange peel, banana peel, potato peel, pomegranate peel and many other different agricultural waste [32]. Some of these materials were chemically or physically modified and others were used in their natural state.

Without any pretreatment (only chopping, drying, grinding and sieving), orange peel was investigated as adsorbent for the removal of Mg, Cu, Mn and Zn, from winery wastewater by Mahajan *et al*. [33]. The maximum adsorption efficiencies of Cu, Zn, Mn and Mg were reported to be 33.35%, 30.26%, 31.92% and 47.5 % respectively. Untreated orange peel was also studied to remove Ni (II) from aqueous solutions by Gönen and Serin [34]. The effect of operational parameters including temperature, time, adsorbent dosage and pH were investigated. The maximum adsorption capacity of Ni was found to be 62.3 mg per gram of adsorbent at pH value of 5.0, and Langmuir model was best fitted at equilibrium time of 14 minutes.

Orange wastes have been utilized for the removal of heavy metals; Pb^{2+}, Cd^{2+} and Zn^{2+}, from binary synthetic mixtures by Pérez-Marín *et al* [35].The maximum adsorption capacity was found to be almost the same for all elements (0.25 mmol/g). Langmuir isotherm efficiently fitted the experimental data at the equilibrium. Adsorption of metals was ordered from maximum to minimum as Pb^{2+}, Zn^{2+}, and Cd^{2+} respectively.

In addition to untreated orange peel, chemically treated, by grafted copolymerization, orange peel was examined for the removal of Cd^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solution by Feng *et al*. [36] . The experiment results showed that maximum adsorption capacity of Cd^{2+}, Ni^{2+}, and Pb^{2+} was 293.3, 162.6, and 476.1 mg/g respectively, and that Langmuir isotherm was best fitted the obtained results. Interestingly, compared to untreated orange peel, the adsorption capacity of Cd^{2+}, Ni^{2+}, and Pb^{2+} increased by 4.6, 16.5, and 4.2- fold respectively.

Ning-chuan and Xue-yi [37] studied the utilization of orange peel as potential adsorbent for the removal of Zn^{2+}, Cu^{2+}, and Pb^{2+} from aqueous solutions. To increase the adsorption capacity, the orange peel was chemically modified with calcium chloride and sodium hydroxide. The effect of pH and initial concentrations on the adsorption efficiency was investigated. It was found that the maximum adsorption capacities of 56.18, 70.73, and 209.8 mg/g for Zn^{2+}, Cu^{2+}, and Pb^{2+} respectively, where Langmuir isotherm was best followed at the equilibrium .

Li *et al*. [38] examined chemically treated orange peel as adsorbent of Cd, Co, Ni, and Zn. The orange peels was treated with several chemicals (acids and alkalis), including NH_4OH, Ca (OH) $_2$, NaOH, H_3PO_4, $C_6H_6O_7 \cdot H_2O$, and $H_2C_2O_4$. The experimental results revealed that Langmuir and Freundlich was followed ,where maximum reported adsorption capacities for Cd, Co, Ni, and Zn were 1.13, 1.23, 1.28, and 1.21 mole/kg respectively . It was noticed that the chemical modification have increased the adsorption capacities by 130%, 178%, 95%, and 60% for Cd, Co, Ni, and Zn respectively.

Table 2.2: Relevant waste materials that have been studied for heavy metals removal

Adsorbent	Adsorbate	type of treatment	Adsorption Capacity	Reference
Orange peel	Mg(II)	Without any pretreatment	47.50%	[31]
	Cu(II)		33.35%	[31]
	Mn(II)		31.92%	[31]
	Zn(II)		30.26%	[31]
	Ni(II)		62.3 mg/g	[32]
	Pb(II)		0.25 mmol/g	[33]
	Cd(II)		0.25 mmol/g	[33]
	Zn(II)		0.25 mmol/g	[33]
	Pb(II)		7.75 mg/g	[38]
	Cu(II)		3.65 mg/g	[38]
	Zn(II)		5.25 mg/g	[38]
	Ni(II)		6.01 mg/g	[38]
	Co(II)		1.82 mg/g	[38]
	Cd(II)	Chemically treated	293.3 mg/g	[34]
	Ni(II)		162.6 mg/g	[34]
	Pb(II)		476.1mg/g	[34]
	Zn(II)		56.18mg/g	[35]
	Cu(II)		70.73mg/g	[35]
	Pb(II)		209.8 mg/g	[35]
	Cd(II)		1.13mole/kg	[35]
	Co(II)		1.23mole/kg	[36]
	Ni(II)		1.28mole/kg	[36]
	Zn(II)		1.21mole/kg	[36]
Mandarin peel	Cu(II)	Without any pretreatment	1.31mmol/g	[36]
	Ni(II)		1.92mmol/g	[37]
	Co(II)		1.37mmol/g	[37]

Table 2.2 (Continued)

Adsorbent	Adsorbate	type of treatment	Adsorption Capacity	Reference
Banana peel	Pb(II)	Without any pretreatment	7.97 mg/g	[38]
	Cu(II)		4.75 mg/g	[38]
	Zn(II)		5.80 mg/g	[38]
	Ni(II)		6.88 mg/g	[38]
	Co(II)		2.55 mg/g	[38]
	Zn(II)		63.23%	[39]
	Pb(II)		92.52%	[39]
	Ni(II)		68.10%	[39]
	Cu(II)		79.55%	[39]
	Cd (II)	Chemically treated	35.52mg/g	[40]
	Cr (VI)		131.56 mg/g	[41]
Banana pith	Hg (II)	Activated Carbon	100%	[42]
	Ni (II)		96.40%	[42]
Pomegranate peel	Cu(II)		97%	[43]
	Pb(II)		92%	[43]
Mango peel	Pb(II)	Without any pretreatment	99.05 mg/g	[45]
	Cd (II)		68.92 mg/g	[45]
Watermelon shell	Cu(II)		111.1 mg/g	[46]
Potato peel	Cu(II)	Carbonization	98.80%	[47]
	Pb(II)	Without any pretreatment	92%	[48]
	Zn(II)		42%	[48]
	Cd (II)		75%	[48]

Table 2.2 (Continued)

Adsorbent	Adsorbate	type of treatment	Adsorption Capacity	Reference
Onion skin	Pb(II)	Chemically treated	93.50%	[49]
	Cu(II)		93.20%	[50]
	Zn(II)		94.20%	[50]
	Cd (II)		98.70%	[50]
	Pb(II)		94.80%	[50]
	Ni(II)		70%	[50]
	Hg(II)		99.81%	[50]
Bone char	Cd (II)	Carbonization	0.57 mmol/ g	[52]
	Cu(II)		0.75mmol/g	[53]
	Zn(II)		0.53mmol/g	[53]
Baker's yeast	Cu(II)	Chemically treated	65 mg/g	[54]
	Pb(II)		192.3 mg/g	[54]

Without any pretreatment rather than grinding and drying, Ponkan mandarin peel was explored as adsorbent for the removal of Cu (II), Ni (II), and Co(II) from aqueous systems by Pavan *et al.* [39]. Based on the experimental results, the adsorption capacities were ordered from minimum to maximum as 1.31, 1.37, and 1.92 mmol/g for Cu (II), Co (II), and Ni (II) respectively at pH value of 4.80, and Langmuir equation was best fitted the obtained results.

Furthermore, without any chemical pretreatment, banana and orange peel were investigated as potential inexpensive biosorbents to remove Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} from synthetic solutions by Annadurai *et al*. [40]. Maximum adsorption capacities for both banana and orange peel were ordered as $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ at pH > 7.0, where Freundlich isotherm was better fitted the results. Maximum adsorption capacities of orange peel were found to be 7.75, 3.65, 5.25, 6.01, and 1.82 mg/g, while for banana peel were 7.97, 4.75, 5.8, 6.88, and 2.55 mg/g for Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+} respectively.

Biosorption of zinc, lead, nickel and copper metal ions from binary and single metal solutions by untreated banana peel was studied by Ashraf *et al.* [41]. The experimental results revealed that the sorption process is proportional to the equilibrium metal concentration. The experiments were conducted with different synthetic concentration solutions. The maximum solution concentration was 150 mg/l, where adsorption capacities reported as 63.23%, 92.52%, 68.10%, and 79.55%, while at minimum concentration (25 mg/l), the adsorption capacities were 84.63%, 94.80%, 82.36%, and 86.81% for zinc, lead, nickel and copper respectively. Langmuir and Freundlich models were successfully fitted at the equilibrium.

The removal of Cd (II) and Cr (VI) ions by chemically modified banana peel from aqueous solutions has been investigated by Memon *et al.* [42], [43] respectively. The experiments was conducted as a function of pH, time, and initial concentration. The maximum removal of Cd (II) was 35.52mg/g at pH value of 8.0, while for Cr (VI) was 131.56 mg/g at pH value of 2.0. The Langmuir adsorption model was followed for Cd (II) adsorption whereas Langmuir and Dubinin–Radushkevich (D–R) were followed to describe Cr (VI) removal behavior.

Activated carbon prepared from banana pith has been employed for the removal of Hg (II) and Ni (II) from aqueous solutions by Kadirvelu *et al.* [44]. The experimental results revealed that at optimum conditions (pH value of 5.0), the maximum removal of Hg (II) was reported as 100% and 96.40 % for Ni (II). It was noticed that the maximum removal of Ni was occurred after 24 hours of contact.

Activated carbon derived from pomegranate peel has been employed for the removal of copper (II) and lead (II) from aqueous solutions by El-Ashtoukhy *et al*. [45]. Three methods were performed for biosorbent preparation; untreated raw material, carbonized material, and chemically activated with $ZnCl_2$ and H_3PO_4 material. The experimental results indicated that maximum adsorption capacity observed when using chemically activated carbon with $ZnCl_2$ at pH value of 5.8 and 5.6 for Cu (II) and Pb (II) respectively. The maximum removal was reported as 97, and 92% for Cu (II) and Pb (II) respectively. Langmuir isotherm was best fitted the experimental data.

Lemon peel and resin were employed as cation exchanger materials for heavy metals removal from synthetic solutions by Arslanoglu *et al*. [46]. The raw materials

were thermally treated. The experimental analysis indicated that metal ions were attracted to lemon resin more efficiently than lemon peels. The removal efficiencies were ordered from maximum to minimum as Pb, Cu, Ni, Fe, Cd, Zn, Co and Mn respectively, where maximum removal of Pb was reported as 0.87 mmol/g while minimum removal of Mn was found to be 0.43 mmol/g.

Untreated mango peel was used by Iqbal *et al*. [47] for the removal of Pb^{2+} and Cd^{2+} from aqueous solutions. The maximum removal of Pb^{2+} and Cd^{2+} was found to be 99.05 and 68.92 mg/g respectively. Kinetic studies showed that heavy metals removal occurred quickly within the first 60 min, and that Langmuir isotherm was satisfactory fitted the results at the equilibrium.

Without any pretreatment rather than drying and grinding, watermelon shell was studied as low cost adsorbent of cupper (II) from aqueous solutions by Banerjee *et al*. [48]. Maximum adsorption capacity was reported as 111.1 mg/g at pH value of 8.0. It was observed that as the pH value increases the adsorption capacity increases until it reach pH value of 8.0, and then decreases again. Langmuir adsorption formula was used to determine the maximum adsorption capacity.

Also Cu (II) removal by potato peel based carbon was tested by Aman *et al*. [49]. The carbonization was conducted in a temperature of 700 ^{o}C. The experimental results interestingly indicated that about 98.8 % of Cu was removed at pH value of 6.0. Freundlich and Langmuir models was used to describe the equilibrium data.

Potato peel also investigated as potential low cost adsorbent for the removal of Pb (II), Zn (II), and Cd (II) by Taha *et al*. [50] .The biosorbent was prepared under low

temperatures (298- 333) K. The experimental investigations showed that the optimum adsorption capacities was found to be 92%, 42%, and 75% for Pb (II), Zn (II), and Cd (II) respectively, which were ordered as Zn(II) < Cd(II) < Pb(II).

The adsorption of lead ions on pretreated onion skin was evaluated by Saka *et al.* [51]. In this study two pretreatment methods were achieved; boiled onion skins (PTOS) and formaldehyde-treated onion skins (FTOS). The experimental results indicated that the optimum removal of Pb was 200 mg/g (93.5%), which was observed for (FTOS) at pH value of 6.0, while for (PTOS) maximum removal was 84.80%. The pseudo-first order kinetic model was followed whereas the best fitted isotherm was Freundlich model for (PTOS) and Langmuir for (FTOS).

Treated onion skin with formaldehyde also investigated for the removal of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} and Hg^{2+} by Kumar and Dara [52]. Based on the Column experiments equilibrium studies, the maximum removal of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} and Hg^{2+} from aqueous solutions were found to be 93.2, 94.2, 98.7, 94.8, 70.0, and 99.81% respectively.

2.8.2 Non-agricultural household organic waste

Non-agricultural household organic waste has been investigated as potential low cost locally available biosorbent for the removal of several heavy metals by many researchers. Removal of Cd^{2+}, Cu^{2+} and Zn^{2+} from multi component system using bone char as low-cost adsorbent was tested by Ko *et al*. [53]. The Sips isotherm was best fitted the data at the equilibrium. The experimental investigations revealed that the adsorption capacities ordered as $Cu^{2+} > Cd^{2+} > Zn^{2+}$.

Bone char derived from animal crushed bones through carbonization process (500 - 700^0) C was examined as adsorbent of cadmium by Cheung *et al*. [54]. The removal cadmium metal ions was found to be 0.57 mmol/ g onto bone char. The kinetic studies reported that Elovich equation was the best model to describe the adsorption process. Moreover, bone char was used by the same authors, [55], to remove zinc and copper ions from aqueous solution. The maximum removal efficiencies were reported as 0.53 and 0.75 mmol/g for zinc and copper respectively, and that Langmuir–Freundlich (L–F) isotherm was best fitted the obtained results at the equilibrium.

Yu *et al.* [56] investigated chemically modified baker's yeast for the removal of $Cu^{2+}$and Pb^{2+} from aqueous solution in the existence of excessive concentration of Na^{+}, Mg^{2+}, Ca^{2+},and K^{2+}. Due to the chemical modification, better and fast adsorption capacity was observed (10-15 times higher than untreated adsorbent), where maximum removal of Cu^{2+} and Pb^{2+} were found to be 65.0 and 192.3 mg/g respectively at pH value between 2.70 and 6.0.

2.8.3 Mixed waste materials

In the published literature, single waste materials as were the most investigated as low cost source of activated carbon, so there is a lack of using mixed waste material, and only few studies were investigated. Activated carbon was prepared from three waste materials; paper, plastic, and palm by Habila *et al.*[7]. The waste materials were mixed by weight with equal ratio, and carbonized, then activated chemically using $Ca(OH)_2$ as activating agent. Finally, used for Tartrazine dye removal, where maximum adsorption capacity was 74.9 mg/g.

Five waste materials from municipal solid waste (MSW) were investigated as low cost source of activated carbon by Song *et al.* [57]. Pine wood, acrylic textile, waste tire, paperboard, and polyvinyl chloride (PVC) were paralyzed in single component, double and triple component mixture. For the triple component, the best adsorption capacity of MB was observed (300 mg/g) when mixing acrylic textile, waste tire, and pine wood with equal ratio, where the surface area was reported as 646.32 m^2/g. For double component, the best mixture was observed when mixing tire waste and pine wood. The waste materials were carbonized and activated in one single step using KOH as activating agent, and the best temperature that gave the highest adsorption capacity and surface area was 800 C^o.

Based on the above extensive literature review, it was noticed that the use of single waste materials for heavy metals removal is very well documented. However, up to the knowledge of the investigator there is a lack of information regarding the utilization of randomly mixed waste materials , particularly, household organic waste (HOW) in the production of activated carbon for heavy metal removal.

CHAPTER 3

MATERIALS AND METHODS

This section explains in details about raw materials which used for the preparation of AC, chemical reagents and methods followed to get the goals of the study. Methods of characterization of raw materials (HOW), activated carbon preparation and characterization, and application of AC in Cd (II), and Pb (II) removal from synthetic solutions will be mainly described.

3.1 Materials

3.1.1 Household Organic Waste (HOW)

Household organic waste (HOW) was collected from different houses in the eastern province in Saudi Arabia. Usually household organic waste is mixed with non-organic waste, for example, plastic, which cannot be composted, so it was separated to avoid any non-organic materials. The obtained household organic waste composed of varying quantities of the following materials; orange peel, banana peel, mango peel and stones, lemon peel, melon and watermelon shells, potato peel, onion and garlic shells, bread crumbs, bone waste of fish and animals, cooked rice remains, egg shells, and others. The collected waste materials (HOW) were mixed well and washed thoroughly with distilled water to remove any physically adhered material, then dried in an air oven at 110 °C for 24 hours. The dried materials were then crushed by using a universal

cutting mill “pulverisette 19” to obtain a final fineness of the waste materials to be about 0.40 mm.

3.2 Methodology

The experimental approach of this study consists of two main phases. These phases are household organic waste characterization and laboratory scale experiments. Characterization included measuring the different physical and chemical characteristics of precursor and prepared AC. Laboratory scale experiments were carried out at KFUPM laboratories are designed to explore the potentiality of utilizing the household organic waste (HOW) for the preparation of AC and removal of heavy metals. The combined results of the two phases of investigation will give a clear picture on the potentiality of utilizing (HOW) in the decontamination of industrial wastewaters.

3.2.1 Characterization of Precursor

To assess the potentiality of utilizing the household organic waste as precursor of activated carbon for the removal of heavy metals from industrial wastewater, the waste itself must be subjected to different tests. Those tests include the waste general physical and chemical characteristics such as grain size and surface area per weight. Based on the characterization, recommendations on the potentiality of utilizing the waste under investigation as an adsorbent of heavy metals will be drawn out.

3.2.1.1 Thermogravimetric Analysis

The variation of the weight-loss with regard to heat range due to the discharge of surface surrounded water and release of volatile matter is clearly described with

Thermogravimetric analysis (TGA). TGA of raw material (HOW) was conducted by a Thermogravimetric analyzer (SDT Q600 V20.9 Build 20). About 45 mg of the (HOW) was taken in alumina crucible and exposed to pyrolysis under N_2 circulation (100 ml/min) from 50 up to 1000 C^o with warming amount, 10 C^o/min.

3.2.1.2 Proximate and Ultimate Analysis

Proximate and ultimate analysis were conducted for the raw material (HOW) as well as for prepared AC. Detailed procedure of the analysis was described in the characterization of AC section 3.2.3.

3.2.2 Preparation of Activated Carbon

10 g of the dried crushed (HOW) materials were mixed thoroughly with 20 ml of in varying impregnations of the activating agents; KOH and H3PO4. The impregnation process was performed at room temperature for 1 hr. to accomplish well penetration of the activating agent into the internal of the (HOW). For activated samples wit phosphoric acid, impregnation of 20 ml of several concentrations of H_3PO_4 (30, 40 and 50 %) was investigated, while impregnation ratios of (0.5, 1.0, and 1.5) were used for KOH Table 3.1. Then, the impregnated sample was dried overnight in the oven at 110°C. The slurry was moved into stainless steel tubes of 300 mm length and 50 mm diameter with two ports of 8 mm diameter and two removable lids at both ends. The tubes were positioned inside a muffle furnace and initially heated at a slower rate (5°C/min), to allow free evolution of volatiles up to hold the required temperature. Soaking at ultimate temperature was performed for different durations. The cooled mass was thoroughly and repeatedly washed with hot distilled water to remove the trace of the activating agent

until the washings shows neutral pH value. Then, the samples were placed in the oven at 110°C for 24 hours. Finally, they grounded and sieved to particle size less than 0.30 mm, and kept in tightly closed bottles ready for use. Figure 3.1 shows a schematic diagram of producing activated carbon from household organic waste.

Table 3.1: Activation Chemicals to be investigated

No.	Chemical	Impregnation
1	KOH	0.5,1.0, and 1.5 (wt/wt)
2	H_3PO_4	30%, 40%, and 50 %(wt.)

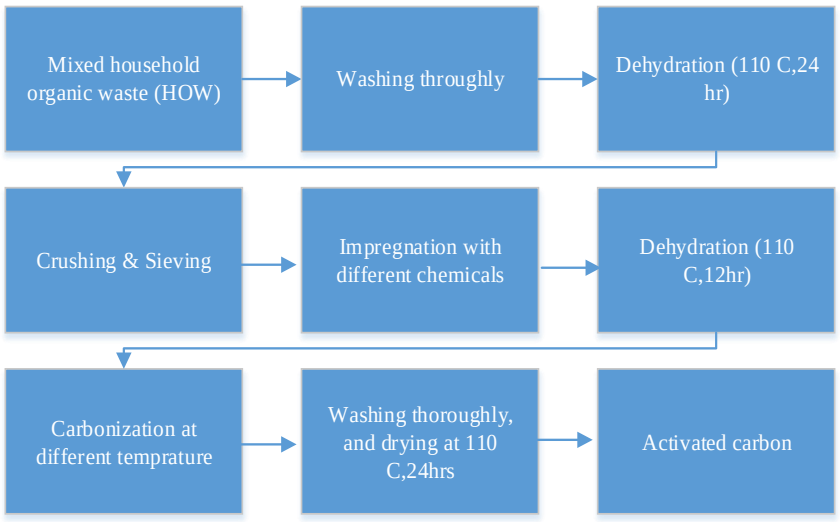


Figure 3.1: Flow diagram for the preparation process of activated carbon from household waste (HOW)

3.2.2.1 The Effect of Impregnation

The effects of impregnation ratio of the activating agents on the produced activated carbon characteristics was investigated. For KOH impregnation ratio of 1:0.5, 1:1, and 1:1.5. The impregnation ratio was identified as weight of the raw material (HOW) to weight of activating agent. Predetermined volume of different concentrations varies from 30% to 50 %(wt. /wt.), were investigated when using H_3PO_4 as activating agent.

3.2.2.2 Effect of Carbonization Temperature

During the activation process, the most impacting aspects for the expansion of porosity is carbonization temperature [55,56]. Carbonization temperatures from 200 to 700 C^o were investigated to study the effect of temperature on the characteristics of the prepared activated carbon.

3.2.2.3 The Effect of Holding time

The effects of holding time on the characteristics of produced activated carbon was investigated. The samples were left in the furnace at final temperature for 60, 90 and 120 minutes. Table 3.2 & Table 3.3 shows different parameters that will be investigated in the production of activated carbon from household organic waste.

Table 3.2 : Parameters to be investigated in activated carbon production with KOH

Sample No	Activating agent	Temperature C^0	Impregnation Ratio(IR)	Time Hour
1	KOH	200	1:0.5	1
2	KOH	200	1:1.5	1
3	KOH	600	1:0.5	1
4	KOH	600	1:1.5	1
5	KOH	200	1:0.5	2
6	KOH	200	1:1.5	2
7	KOH	600	1:0.5	2
8	KOH	600	1:1.5	2
9	KOH	400	1:1	1.5
10	KOH	400	1:1	1.5
11	KOH	400	1:1	1.5

Table 3.3: Parameters to be investigated in activated carbon production with H_3PO_4

Sample No	Activating agent	Temperature C^0	Concentration	Time Hour
12	H3PO4	200	30 % wt.	1
13	H3PO4	200	50 % wt.	1
14	H3PO4	600	30 % wt.	1
15	H3PO4	600	50 % wt.	1
16	H3PO4	200	30 % wt.	2
17	H3PO4	200	50 % wt.	2
18	H3PO4	600	30 % wt.	2
19	H3PO4	600	50 % wt.	2
20	H3PO4	400	40 % wt.	1.5
21	H3PO4	400	40 % wt.	1.5
22	H3PO4	400	40 % wt.	1.5
23	H3PO4	300	30 % wt.	1
24	H3PO4	300	50 % wt.	1
25	H3PO4	300	30 % wt.	2
26	H3PO4	300	50 % wt.	2
27	H3PO4	500	30 % wt.	1
28	H3PO4	500	40 % wt.	1
29	H3PO4	500	50 % wt.	1
30	H3PO4	500	30 % wt.	2
31	H3PO4	500	40 % wt.	2
32	H3PO4	500	50 % wt.	2
33	H3PO4	700	30 % wt.	1
34	H3PO4	700	50 % wt.	1
35	H3PO4	700	30 % wt.	2
36	H3PO4	700	50 % wt.	2

3.2.3 Characterization of AC

The following standard procedures were employed to characterize different properties of the prepared activated carbon from household organic waste (HOW).

3.2.3.1 Proximate Analysis

ASTM D2867 – 09 oven-drying test method was used to find the moisture content of A.C and raw material, about 1.5 g of powder activated carbon was put in dried and accurately weighted crucible with lid. The crucible with sample was opened and put in the dry oven at 150 C^o and left for 3.0 hrs, with its lid. After that the crucible is taken out, closed, and cooled in desiccator to the room temperature and weighted again. The moisture content was calculated using the following equation:

$$Moisture\ (\%) = \frac{\text{Loss in weight due to drying}}{\text{Intial sample weight}} * 100 \qquad (3.1)$$

ASTM D2866-94 test method was used to find the ash content of the raw material (HOW) and A.C [60]. An empty clean crucible was heated in a muffle furnace at 500 C^o, cooled in desiccator to the room temperature and weighted, about 1.5 g of raw material (HOW) and powder activated carbon was put in the crucible and weighted again. The crucible with sample was located in a cool muffle furnace and the temperature set at 500 C^o. Once the required temperature was reached, the crucible is taken out and cooled in desiccator to the room temperature and weighted again. The ash material was computed using the equation:

$$Ash\ content\ (\%) = \frac{\text{Ash weight}}{\text{Oven dry weight}} * 100 \quad (3.2)$$

Volatile matter was determined following (ASTM D5832 – 98), where the AC sample was heated to 950 C and then the weight loss was considered as volatile matter, using the following formula:

$$Volatile\ matter(\%) = \frac{\text{Volatile component weight}}{\text{Oven dry weight}} * 100 \quad (3.3)$$

The fixed carbon percentage was computed by subtracting moisture content, ash content, and volatile matte from 100 as following:

$$Fixed\ carbon(\ \%) = 100 - (moisture\ \% + Ash\ \% + volatile\ matter\% \ ) \quad (3.4)$$

3.2.3.2 Ultimate Analysis

CHNS analyzer (2400 Series II CHNS/O Analyzer (PerkinElmer, CT, USA)) was used to carry out the elemental analysis for the raw material (HOW) and the prepared AC. The oxygen percentage was computed by subtracting the percentage of C, H, N and S from 100 as following,

$$Oxygen(\%) = 100 - (N(\%) + C(\%) + H(\%) + S(\%)) \quad (3.5)$$

3.2.3.3 Yield

The yield of produced activated carbon was computed based on ratio of the resulted activated carbon to the dried raw material (HOW) as shown in the following formula:

$$Yield(\%) = \frac{weight\ of\ produced\ activated\ carbon}{weight\ of\ raw\ material\ (HOW)} \tag{3.6}$$

3.2.3.4 Bulk density

A pycnometer was used to measure the bulk density of the AC sample. First, specific amount of AC was put in the pycnometer and the weight of AC and the pycnometer was recorded. Then, the pycnometer was filled up with water and weighted. The weight of water was calculated from the difference in weight before and after adding water. The volume of added water was computed form density law ($V_W=m_w/p_w$), from which the volume of AC was calculated from the difference between the volume of added water and the volume of empty pycnometer. The bulk density of AC was calculated using the density formula (below).

$$\begin{aligned} volume\ of\ A.C \\ &= Volume\ of\ empty\ \text{pycnometer} \\ &- \text{volume of added water} \end{aligned} \tag{3.7}$$

$$Bulk\ density = \frac{m\ (AC)}{V(AC)} \tag{3.8}$$

3.2.3.5 Porosity Characterization

Standard multi point BET method [61] was used to investigate the porous characteristics of the prepared A.C samples, including specific surface area, pore size, and pore volume. N_2 adsorption isotherms at 77 K were conducted on the prepared samples using an automatic adsorption unit (Micrometric, ASAP 2020 V3.05 H). To eliminate any possibly desorbed moisture or contaminants from the surrounded atmosphere, the AC sample was degassed at 200 C^o for 90 minutes prior to analysis.

3.2.3.6 Surface Chemistry Characterization

Fourier Transform Infrared (FTIR) spectroscopy technique was applied to determine the surface functional groups of the raw materials (HOW) and A.C samples using (Thermo Electron Corporation Nicolet Nexus 670 FT-IR Spectrometer). FTIR spectra of raw material (HOW) and AC sample were reported within 500 – 4000 cm^{-1}. KBr pellet was used for recording the transmission spectra of (HOW) and A.C samples. Prior to the analysis, dry KBr was mixed and grinded thoroughly with very small amount of the sample (1-2) % in mortar. Then the mixture was hydraulically pressed to form transparent and homogeneous pellet, which was positioned in the IR sample holder and analyzed.

3.2.3.7 Microscopy

Scanning Electron microscope (SEM) was used to examine surface morphology which shows the shapes and sizes of pores on sample surface of raw material (HOW) and AC. (EDS) Energy dispersive spectrometer were used for investigating the elemental surface composition of raw material (HOW) and AC sample.

3.2.3.8 X-ray diffraction spectroscopy

Crystalline structures of raw material (HOW) and AC were examined by X-ray diffraction technique (XRD), where (Ultima IV) X-ray diffractometer was employed for this purpose. Scan run was conducted in the range angle from 10^{o} to 80^{o}, with a step size of 0.02^{o}/s.

3.2.3.9 Methylene blue Removal

Methylene blue number is a good indication of the porous structure present in AC [62], so the adsorption of methylene blue was conducted for all prepared A C and raw material (HOW) to draw the line of the best preparation conditions. A 50 ml volume of 100 ppm MB solution was put in contact with 0.1 g of sample in 125ml Erlenmeyer flask and put in the shaker at 200 rpm at room temperature for 2 hrs. The experimental conditions were determined based on preliminary study. The samples were filtered using Whatman Grade 42 filter paper and analyzed with double-beam UV spectrometer (Shimadzu 1650PC: UV-visible Spectrophotometer). The adsorption capacity of MB (was calculated as following:

$$qe(mg/g) = (Co - Ct) * \frac{V}{m} \tag{3.9}$$

Where Co and Ct are the initial and residual concentration of MB (mg/l) respectively, V is the volume of the solution (L), m is sample mass (g). Adsorption efficiency was also calculated using the following formula:

$$Removal\ effeciency = \frac{Co - Ct}{Co} * 100 \tag{3.10}$$

3.2.4 Adsorption Experiments

Single and competitive adsorption experiments of Cd (II) and Pb (II) in batch mode were conducted in order to evaluate the adsorption capacity of the household organic waste (HOW) based activated carbon. A stock solutions of 1000 mg/l of Cd (II) and Pb (II) were prepared from nitrate salts by dissolving 2.744 g and 1.5984 g of $Cd(NO_3)_2.4H_2O$ and Pb ($(NO_3)_2$ respectively, in 1.000 ml of deionized water. Before making up to 1000 ml, the stock solutions were acidified by adding HNO_3 until pH < 2.0. A proper dilutions were carried out to prepare different concentrations from the stock

$$C_1 * V_1 = C_2 * V_2 \quad (3.11)$$

solution using the following formula:

A 50 ml volume of different concentrations of single and binary metal solutions was put in contact with certain amount of AC in 125 ml Erlenmeyer flask and placed in the shaker at constant shaking of 200 rpm at room temperature. At the end of each specified shacking time, the samples were filtered through filter paper (Whatman Grade 42) and acidified with nitric acid to make the samples ready for analysis of metals content.

3.2.4.1 Methods of Analysis

The standard methods were used for the analysis of the samples. Each experiment was carried out in duplicates in order to obtain reliable results. Blank samples were also included in each run, where no AC was added to the synthetic wastewater. Atomic Absorption Spectroscopy AAS (PerkinElmer, Analyst 700) was used to measure the

initial and remaining concentrations of the metal ions. The adsorption capacity for each sample was calculated as following:

$$qe(mg/g) = (Co - Ct) * \frac{V}{m} \quad (3.12)$$

Where Co and Ct are the initial and residual concentration of metal ions (mg/l) respectively, V is the volume of the solution (L), m is adsorbent mass (g). Removal efficiency was also calculated using the following formula:

$$Removal\ effeciency = \frac{Co - Ct}{Co} * 100 \quad (3.13)$$

3.2.4.2 Effect of operational parameter

The effect of different operational parameter, including initial concentration, adsorbent dosage, pH, and contact time on the adsorption process was investigated in this study.

3.2.4.2.1 Effect of pH

Adsorption process is strongly pH dependent, therefore, the effect of pH on the adsorption process was investigated by using pH values of 3.0, 4.0, 5.0, 5.5, 6.0, and 7.0. The pH values were adjusted using 0.1 N of HNO_3 and 0.1 N of NaOH. Batch experiments were conducted by adding 50 mg of AC to 50 ml of 100 mg/l of metal solution in 125 ml Erlenmeyer flask at different pH values. Then, the samples were placed in the shaker for 3.0 hours at constant shaking of 200 rpm at room temperature.

3.2.4.2.2 Effect of contact time

The effect of contact time on the removal efficiency of heavy metal ions from single and binary aqueous solutions by the prepared activated carbon was investigated. Batch experiments were conducted by adding 50 mg of AC to 50 ml of 100 mg/l of single and binary metal solutions in 125 ml Erlenmeyer flask at pH value of 5.0. Then, the samples were placed in the shaker for different time intervals, namely 5, 10, 15, 30, 120, 240, and 480 minutes at constant shaking of 200 rpm at room temperature.

3.2.4.2.3 Effect of Initial concentrations

The effect of the initial concentration on the adsorption of single and binary metal ions from synthetic aqueous solutions by the prepared activated carbon was evaluated. Batch experiments were conducted by adding 50 mg of AC to 50 ml of different concentrations of metal solutions in 125 ml Erlenmeyer flask at pH value of 5.0. Then, the samples were placed in the shaker for 3 hours. In single adsorption experiments, the investigated initial concentrations were 25, 50, 100, 150, 200, and 300 mg/l. The studied initial concentrations of competitive adsorption (mg/l) are shown in

Table 3.4, where first concentration for cadmium while second one for lead. For example, concentration of (25, 50) means the concentration of cadmium in the solution is 25 and for lead is 50 mg/l.

Table 3.4: Intial concentrations of competetive adsorption experiments

Pb(II) / Cd(II)	25	50	100	150	200	300
25	(25,25)	(25,50)	(25,100)	(25,150)	(25,200)	(25,300)
50	(50,25)	(50,50)	(50,100)	(50,150)	(50,200)	(50,300)
100	(100,25)	(100,50)	(100,100)	(100,150)	(100,200)	(100,300)
200	(200,25)	(200,50)	(200,100)	(200,150)	(200,200)	(200,300)
300	(300,25)	(300,50)	(300,100)	(300,150)	(300,200)	(300,300)

3.2.4.2.4 Effect of adsorbent dosage

Numerous amount of AC was used to investigate the effect of adsorbent dosage on the adsorption process in single and binary systems. To do this, batch experiments were conducted by adding various adsorbent dosage; 25, 50, 100,200, and 300 mg to 50 ml of 100 mg/l of metal solutions in 125 ml Erlenmeyer flask at pH value of 5.0. Then, the samples were placed in the shaker for 3.0 hours at constant shaking of 200 rpm at room temperature. Table 3.5 summarizes the operational parameter that were conducted throughout this study.

Table 3.5: Operational parameters that were conducted in this research

Metal	**Cd (II), Pb(II), (Cd(II +Pb (II))**
Initial Concentration (mg/l)	**25,50, 100, 150,200, and 300**
Adsorbent dosage (mg)	**(25, 50, 100,200 and 300 per 50 ml)**
pH	**3.0,4.0, 5.0,5.5, 6.0, and 7.0**
Time (minutes)	**5.0 ,10 ,15 ,30 ,60 ,120 ,240 , and 480**

CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation and Characterization of Activated Carbon

4.1.1 Overview

The raw material, household organic waste (HOW), was characterized to evaluate its potentiality for the production of activated carbon. Activated carbon was prepared through chemical activation process, with two activating agents, namely KOH and H_3PO_4. Influence of different operational parameters, including temperature, time, and impregnation on the porous structure of the prepared samples has been determined by isotherms of N_2 gas adsorption (BET). Due to limited resources the BET analysis was conducted for only few samples (5), so the best preparation conditions were estimated based on three criteria; yield of AC, adsorption of MB, adsorption of heavy metals, and BET surface area. The best produced AC was used for removal of Cd (II) and Pb (II) from synthetic wastewater under the effect of different adsorption parameter.

4.1.2 Characterization of Precursor

The results of proximate and ultimate analyses that were carried out for the household organic waste (HOW) are shown in table 4.10, the results of ultimate analysis by CHNS analyzer revealed that the raw material contains of negligible amount of sulfur

and law nitrogen, while high carbon and oxygen content were observed. The profile of Thermogravimetric analysis (TGA) of raw material (HOW) is illustrated in Figure 4.1.

Table 4.1 : Proximate and ultimate analysis of household organic waste (HOW)

Proximate analysis		Ultimate analysis	
Property	Content (%)	Element	Content (%)
Moisture	6.667	C	44.68
Ash	8.6	H	6.8
Volatile	90	N	3.11
		S	0.11
		O	45.3

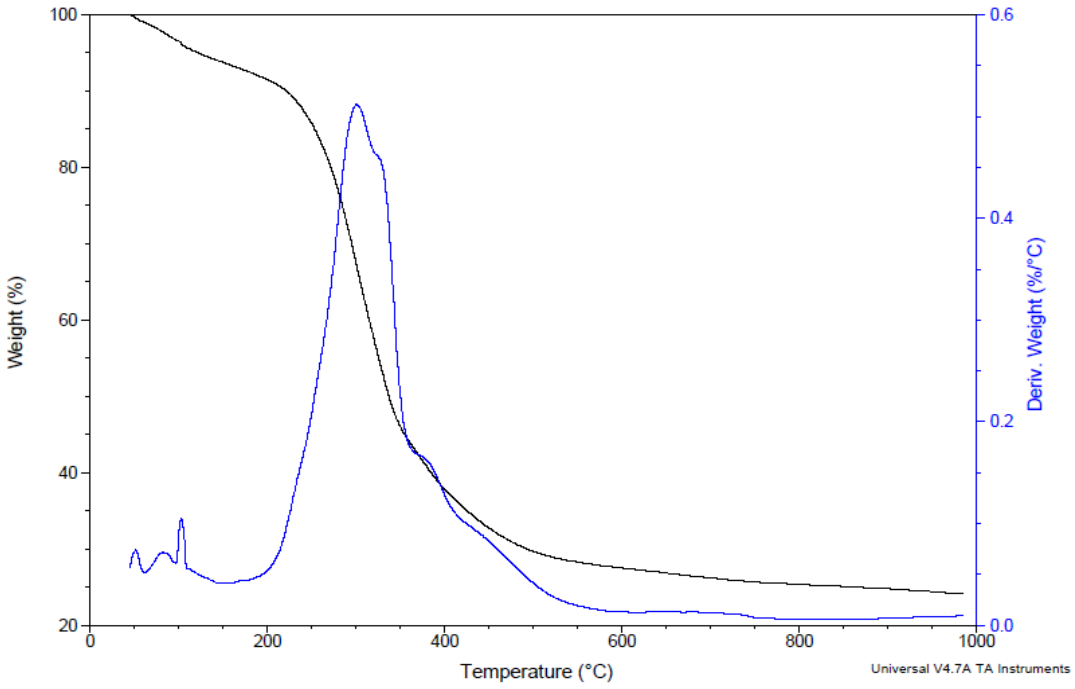


Figure 4.1 : TGA of household organic waste (HOW)

Figure 4.1 : TGA of household organic waste (HOW) shows that when temperature increased from 50 C to about 250 C the weight loss of raw material was about 15 %, due to the release of surface bound water and discharge of moisture, whereas when temperature increased from 250 C to 550 C, dramatically decrease in the sample weight (55 %), which resulted from decomposition of cellulose. Close results was obtained by El-Hendawy *et al.*[63] and Hasan *et al*. [64] who prepared AC from cotton stalks and grape waste respectively.

4.1.3 Activated carbon production process

Activated carbon was prepared using chemical activation process, with two activating agents, namely KOH and H_3PO_4, under different operational parameters, including temperature, time, and impregnation.

4.1.3.1 Effect of Process Parameters

The evolution, of porosity during chemical activation process depends on different process parameters including temperature, time, and impregnation.

4.1.3.2 Effect of Process Parameter on Yield of Activated carbon

Activation temperature plays a key role in activated carbon production process, so the effect of carbonization temperature on the yield, and adsorption capacity of the prepared AC was investigated. Figure 4.2Figure 4.3) shows the effect of carbonization temperature on the yield (%) of the prepared AC samples with phosphoric acid at different temperatures varying from 200 to 700 for different activation durations (60-120) minutes. It was found that, under different conditions, as the temperature increased the yield of AC

decreased. This is can be attributed to the fact that, when temperature increases the thermal decomposition of lingocellulosic material also increases due to the release of volatile matter [65], . At higher activation temperatures, violent gasification due to the conversion of carbon to CO and CO_2, takes place and lead to the loss of considerable amount of carbon because of the volatilization. Alau *et al* [66] studied the effect of temperature on the yield of AC from Neem husk. They reported that the yield of AC decreases with increasing the temperature because of the increase in weight loss due to high volatilization. In this study the lowest yield obtained at the highest temperature (700 C^o), while highest yield (53 %) obtained at the lowest temperature (200 C^o). With increasing temperature to 700 C^o, the yield of AC decreased to 30 %. The low yield at temperature of 200 for 1.0 hour could be attributed to incomplete carbonization of the raw material. The same trends was found by many researchers [63 ,65]. Foo and Lee [65] studied the effect of temperature on the yield of AC prepared from stink bean with H_3PO_4 at different impregnations, and they found that the yield decreased with increasing the temperature.

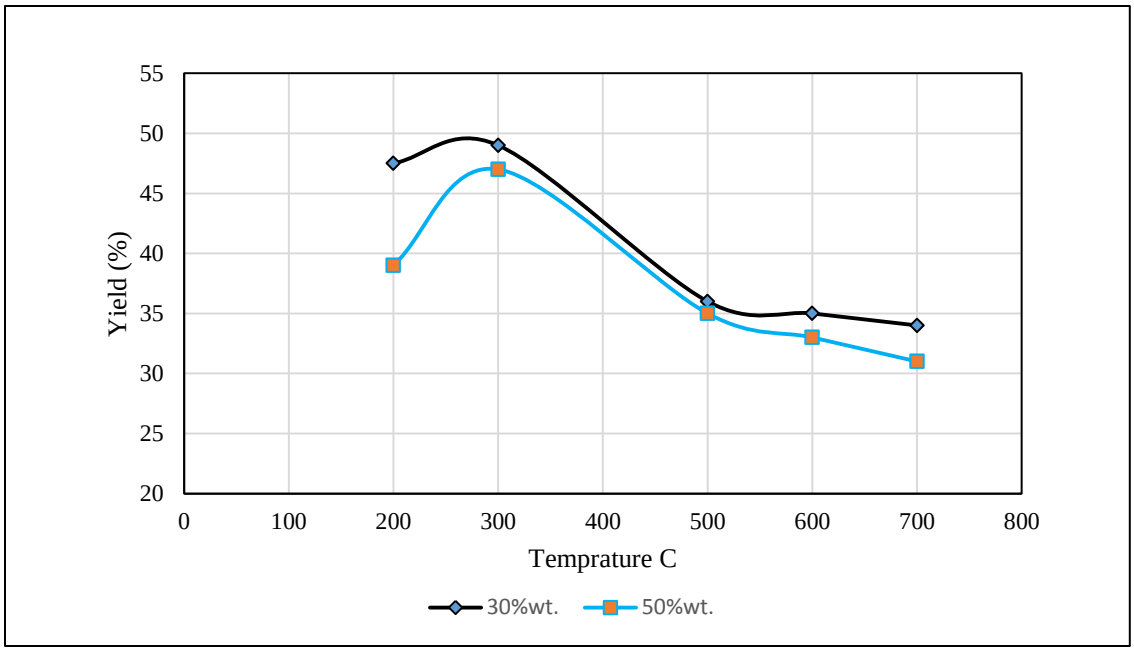


Figure 4.2:Effect of carbonization temperature on the yield of AC prepared with H_3PO_4 at different impregnation ratio and 2.0 hour activation time

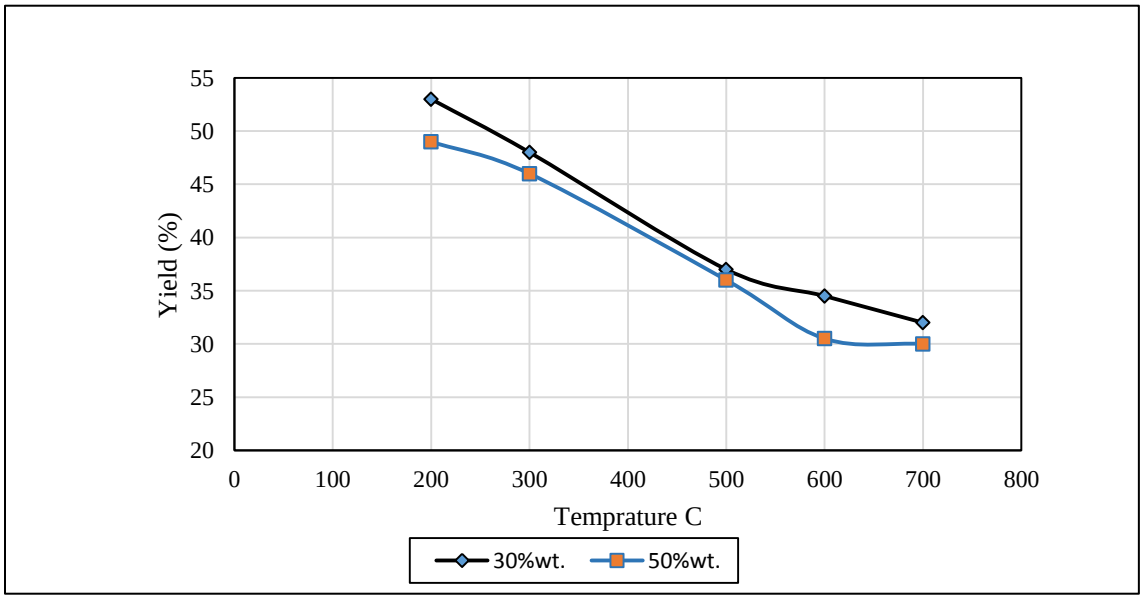


Figure 4.3: Effect of carbonization temperature on the yield of AC prepared with H_3PO_4 at different impregnation ratio and 2.0 hour activation time

The effect of activation temperature on the yield of activated carbon prepared with KOH was also investigated and the results presented in Figure 4.5 & Figure 4.5 . It was observed that the yield of activated carbon was not clearly affected by activation temperature, and only small variation was noticed when increasing the temperature from 200 to 600 C. This means that the impregnation ratio of KOH is the dominating factor affecting the yield of prepared AC. This may attributed to the destructive nature of KOH on the raw materials, regardless of temperature [17]. Consequently, the yield of AC prepared with KOH was much lower than that prepared with H_3PO_4, so wide range of activation temperatures investigated (200, 300, 400, 500, 600, and 700 C) with H_3PO_4 compared to that activated with KOH, where the investigated temperatures were 200,400, and 600.

In addition to the activation temperature, the effect of impregnation ratio of the precursor to the activating agent on the yield of AC also investigated by varying impregnation from 1:0.5 to 1:1.5 for KOH, and 30% to 50 % for H_3PO_4 . As shown in Figures (Figure 4.2Figure 4.3, Figure 4.4Figure 4.5) , in all cases, it was observed that when increasing the impregnation ratio, the yield of AC decreased, because when increasing the concentration of activating agent, the decomposition reaction increases and leads to more release of the tars from the cross linked structure of the raw materials [65]. Wang *et al*. [68] studied the effect of impregnation ratio on the yield of prepared AC from pruning mulberry shoot with phosphoric acid. It was observed that increasing the impregnation ratio from 2:1 to 3:1 decreased the yield of the prepared AC. Furthermore, the effect of impregnation ratio on the yield of prepared AC from cattle-

manure with $ZnCl_2$ was investigated by Qian *et al.* [69] . It was found that the yield of AC gradually decreased by increasing the impregnation ratio from 0.50 to 2.0.

The effect of activation time on the produced activated carbon was also investigated, where activation process was conducted for 1.0, 1.50, and 2.0 hours. Figures (4.60 &4.70) shows the effect of activation time on the yield of prepared AC samples with H_3PO_4. The results obviously shows that the graph yield for one and two hours almost coincide to each other indicating that the activation time at different temperature and concentration has negligible effect on the yield of prepared AC samples. This might because most of the volatilization occurs within the first hour. Similar findings was observed by Malik *et al.* [70] who studied the effect of activation time on the yield of AC prepared from ground shell waste produced from oil mill. They observed no significant change in yield with respect to activation time.

It was concluded that, the yield of AC prepared with H_3PO_4 higher than that prepared with KOH due to the destructive nature of the KOH, when using KOH the highest obtained yield was 12% at activation temperature of 400 C, impregnation ratio of 1:1, and activation time of 1.0 hour and the lowest yield (7%) at the most sever conditions; activation temperature of 600 C,

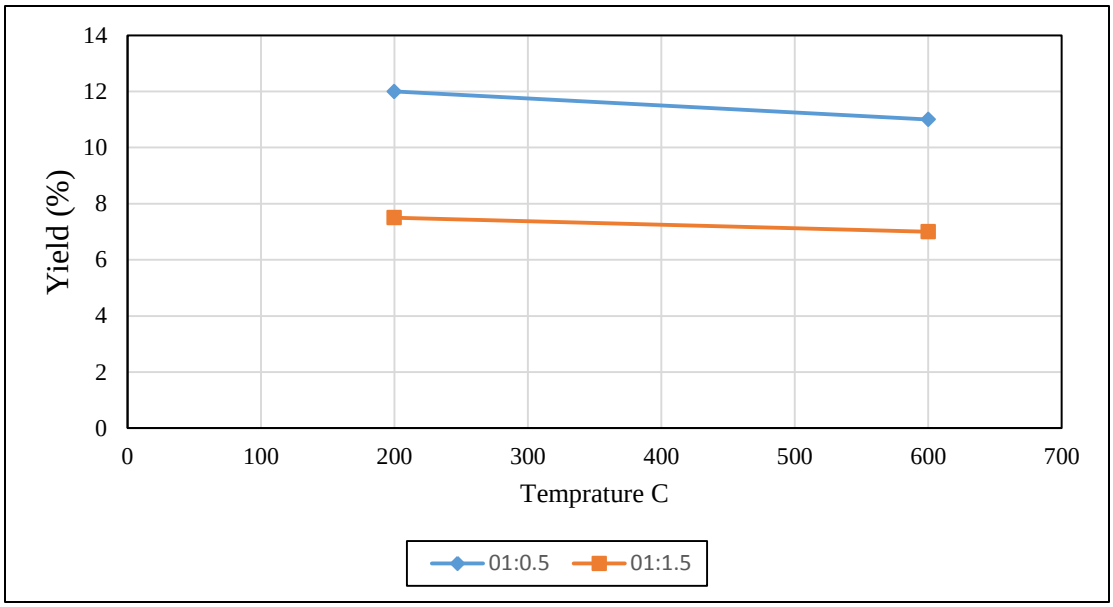


Figure 4.4:Effect of carbonization temperature on the yield of AC prepared with KOH at different impregnation ratio and 1.0 hour activation time

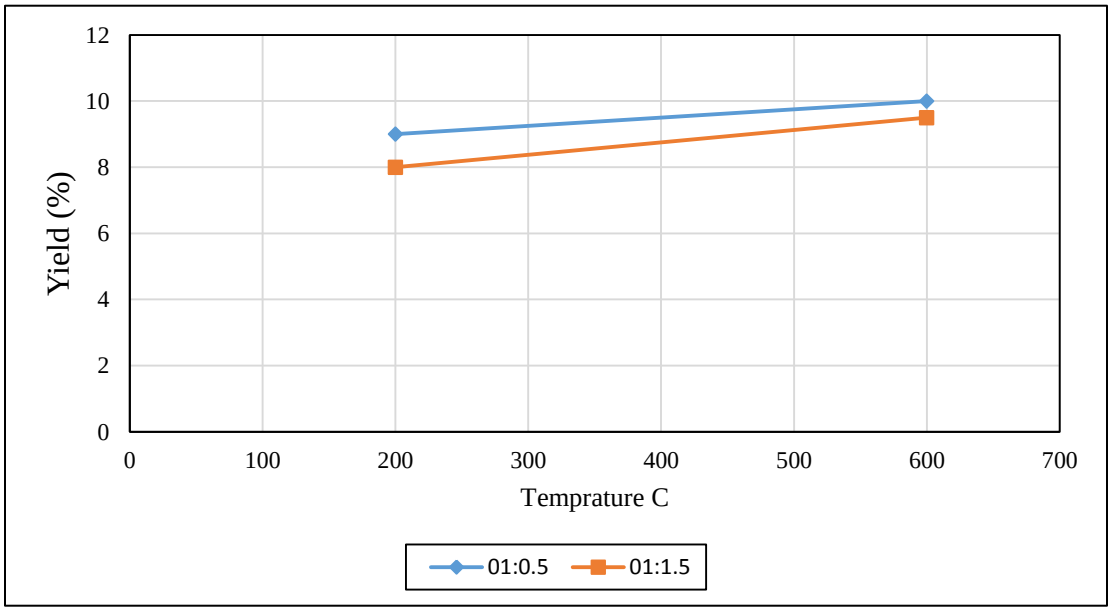


Figure 4.5: Effect of carbonization temperature on the yield of AC prepared with KOH at different impregnation ratio and 2.0 hour activation time

impregnation ratio of 1:1.5, and activation time of 2.0 hours, whereas the highest obtained yield was 53 % at activation temperature of 200 C, concentration of (30 % wt.), and activation time of 2.0 hours and the lowest yield (32%) at the most sever conditions; activation temperature of 700 C, concentration of (50 % wt.), and activation time of 2.0 hours . Furthermore, the surface area of AC prepared with KOH was lower than that prepared with H_3PO_4. For example, at activation conditions of 600 C temperature, 2.0 hours activation time, and impregnation ratio of 1:1.5, and 50% the surface area was around 350 m^2/g, and 700 m^2/g for KOH and H_3PO_4 respectively, Based on these results, and because very law yield obtained of AC samples prepared with KOH, they were excluded from further investigations.

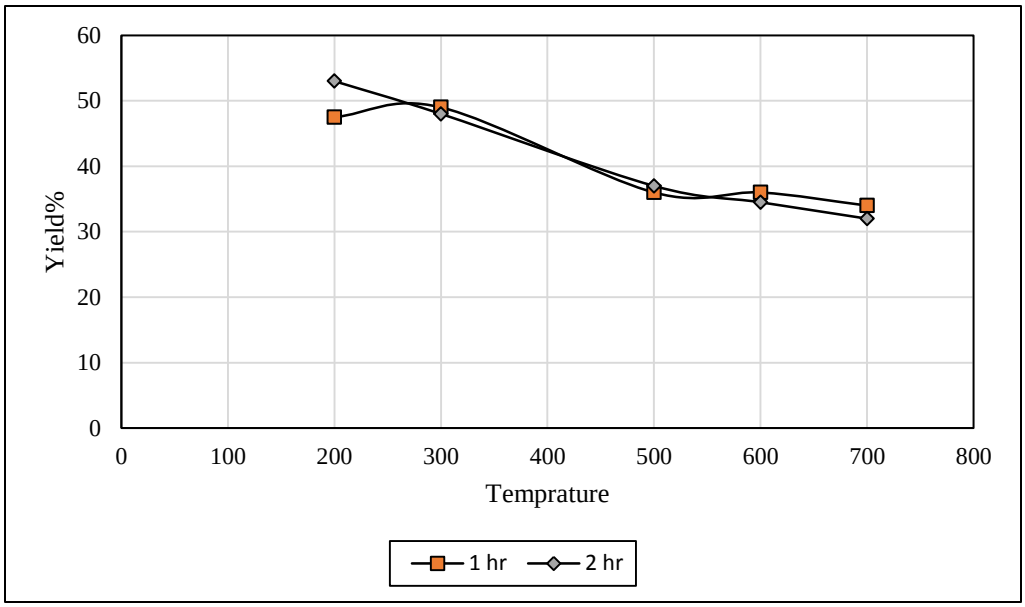


Figure 4.6:Effect of activation time on the yield of prepared AC with 30% H_3PO_4

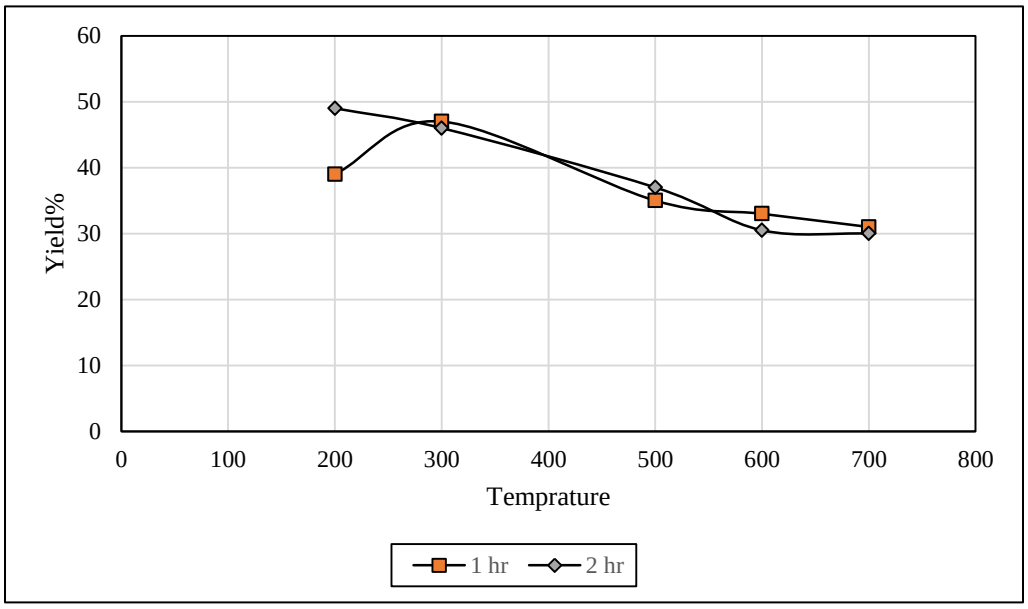


Figure 4.7: Effect of activation time on the yield of prepared AC with 50% H_3PO_4

4.1.3.3 Effect of Process Parameter on removal of methylene blue (MB)

Adsorption of methylene blue is a good indication of the porous structure present in AC [62], so the adsorption of methylene blue was conducted for All samples of AC prepared with H_3PO_4 .The effect of different process parameters on the removal efficiency of MB was investigated for prepared AC. Figure 4.9) illustrates the removal efficiency of MB on the prepared activated samples at activation temperature between 200 and 700, Impregnation ratio from 30% to 50 %, and time between 60 and 120 minutes for samples activated with H_3PO_4 . Increasing the temperature from 200 C to 700 C, for activation time of 1.0 hour enhanced the adsorption efficiency from 3 % to 90 % and from 6% to 100% at 30% and 50 % acid concentration respectively as shown in Figure 4.80. Similarly, increasing the temperature from 200 C to 700 C led to increase the removal efficiency from about 1.5 % to 100 %, for activation time of 2.0 hours as shown in Figure 4.90.

The results revealed that the removal efficiency of MB for the prepared samples was gradually enhanced by increasing the activation temperature, because as temperature increases more release of volatile matter occurs which causes formation of pores on the prepared AC. In addition, the increasing of acid concentration increased the MB removal. Increasing activation time also led to an increasing of MB uptake for the prepared samples, because the increase in , concentration and activation time might led to the increase in porosity due to increase the contact between the raw material and activating agents, close results was also observed by Liou [71] who studied the effect of temperature and impregnation ratio on the adsorption capacity and porous structure of AC prepared from sugar cane bagasse. He reported that the adsorption capacity and

porosity of AC increased when the impregnation ratio increased from 1.0 to 2.0, and temperature from 400 to 500 C^{o}. He attributed this behavior to the same abovementioned reasons.

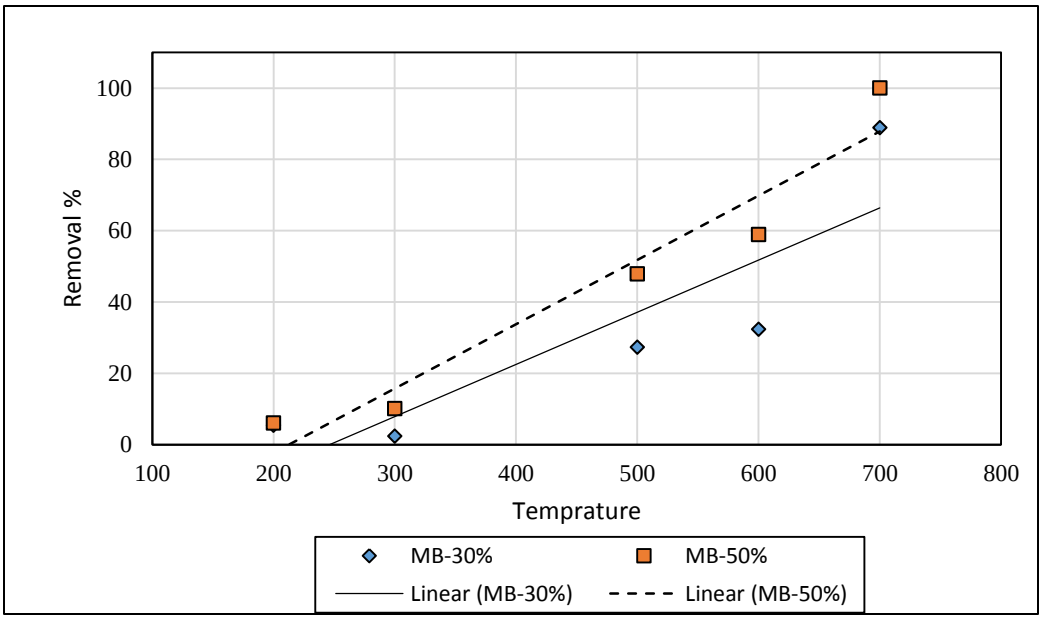


Figure 4.8:Effect of activation parameters on the MB removal for prepared AC with H_3PO_4 for 1.0 hour

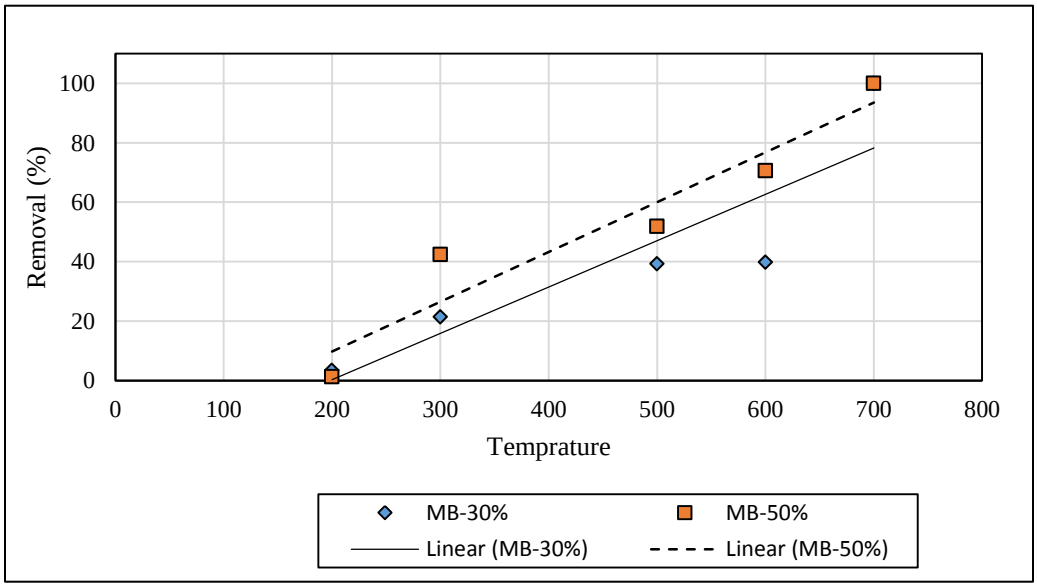


Figure 4.9: Effect of activation parameters on the MB removal for prepared AC with H_3PO_4 for 2.0 hours

Similar findings was also observed by Mdoe and Mkayula [72]. They investigated the effect of temperature and impregnation on the adsorption of MB on AC prepared from rice husks with NaCl as activating agent, they found that as the temperature and impregnation ratio increases, the removal of MB increases. They attributed that to the strong penetration of activating agent at high temperature into the structure of raw material, which in turn increase the surface area. Based on the illustrated results, the porous characteristics of the produced AC is strongly activation temperature dependent, where maximum removal of MB was obtained at the highest temperature. Accordingly, the best condition are; activation temperature 700 C, activation time 120 minutes, and concentration of 30% and 50%., where 100 % removal was observed. However, the adsorption of MB is a good indication of mesoporous structure. Ahmad *et al*. [73] reported that MB molecules can be accessible to pores that have width more than 1.50 nm , so it is not perfectly measure of microporosity or pores less than 1.5 nm, which may present in the prepared AC samples, and since the objective of this research is to produce AC and investigate its performance in heavy metals removal, further investigations were made for the prepared AC samples that removed 70% percent or more from MB.

4.1.3.4 Effect of Process Parameter on removal of heavy metals from synthetic solutions

As mentioned above, further experiments were conducted for prepared AC samples that showed good removal for MB in order to determine the best condition based on the removal of heavy metals. Table 4.2 shows the activation conditions for the investigated samples. Batch experiments were carried out by adding 100 mg of AC to 50 ml of 75 mg/l of Cd (II) solution and 50 mg to 50 ml of 100 mg/l of Pb for the removal of

Cd (II) and Pb (II) respectively in 125 ml Erlenmeyer flask and placed in the shaker at constant shaking of 200 rpm at room temperature. These conditions selected based on preliminary studies. The obtained results are presented in table 4.20. It was observed that for both metals removal Cd (II) and Pb (II), the increasing in activations temperature from 600 C to 700 C led to increase in the removal efficiency. Also for the same temperature and acid concentration, the removal efficiency of prepared samples for both metals increased by increasing the activation time from 1.0 to 2.0 hours, which is in good agreement with MB removal. However, for the same activation temperature and time, the removal efficiency of both metals enhanced by decreasing the concentration of activating agent. At constant activation temperature of 700 C^o, when the acid concentration increased from 30 % to 50%(w/w), the removal efficiency of Cd (II) decreased from about 49% to 43.5 and from about 55% to 53% for 1.0 and 2.0 hours respectively, similarly, the removal efficiency of Pb (II) decreased from about 58.5% to 50 and from about 64% to 59.0% at the same conditions. The reason for the decrease in removal efficiency by increasing the concentration of activating agent may attributed to that high surface area due to creation of microporosity was obtained at 700 C and 30% concentration . However, when the concentration increased to 50 %, the obtained microporosity either destroyed or combining together due to the violent reaction between the precursor and activating agent [74]. Onyeka *et al*. [75] investigated the removal of Cadmium and lead on AC prepared from peanut seed and palm kernel shell with H_3PO_4. It was observed that the removal efficiency of both metals increased when activation temperature increased from 600 to 800 C^o .Örkün *et al*. [76], who studied the effect of impregnation ratio on the porous characteristics of AC prepared from hazelnut shell with

H_3PO_4 , reported that after certain acid concentration where the microporosity is formed, the increase in concentration decreases the porous characteristics due to the formation of wider pores and mesopores. Malik et al [68] studied the effect of the same temperatures on adsorption of iodine on AC prepared from groundnut shell with zinc chloride. They found that the adsorption capacity increased when the temperature increased from 600 to 700 C^o.

Table 4.2 : Activations conditions of investigated samples for metal removal

Sample ID	Activation temperature	Concentration (% wt)	Time (hour)	Yield (%)	MB removal
1	600	50	2	30.5	70.6362
2	700	30	1	34	88.9118
3	700	50	1	31	100
4	700	30	2	32	100
5	700	50	2	30	100

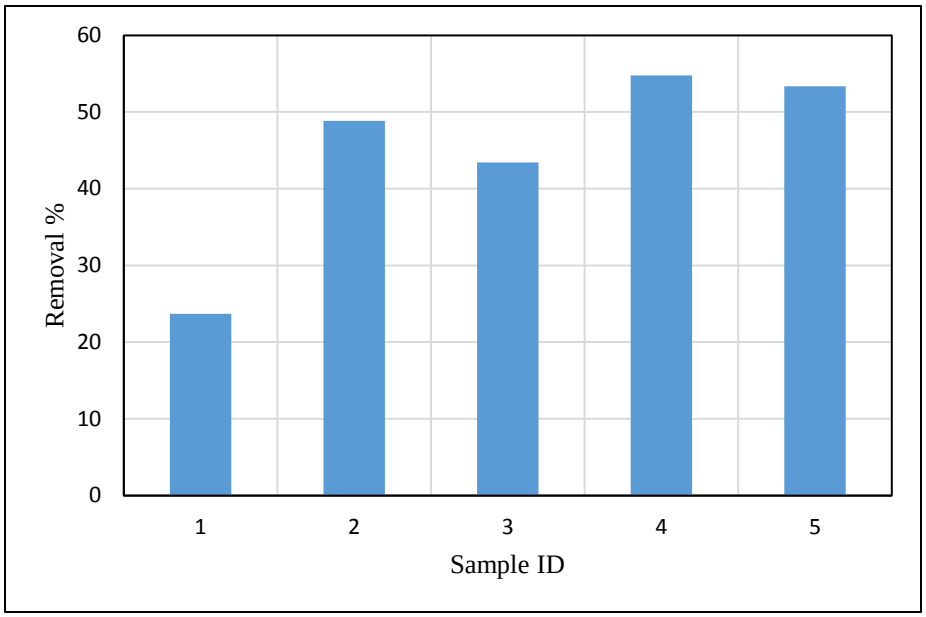


Figure 4.10:Effect of activation parameters on the removal efficiency of Cd (II)

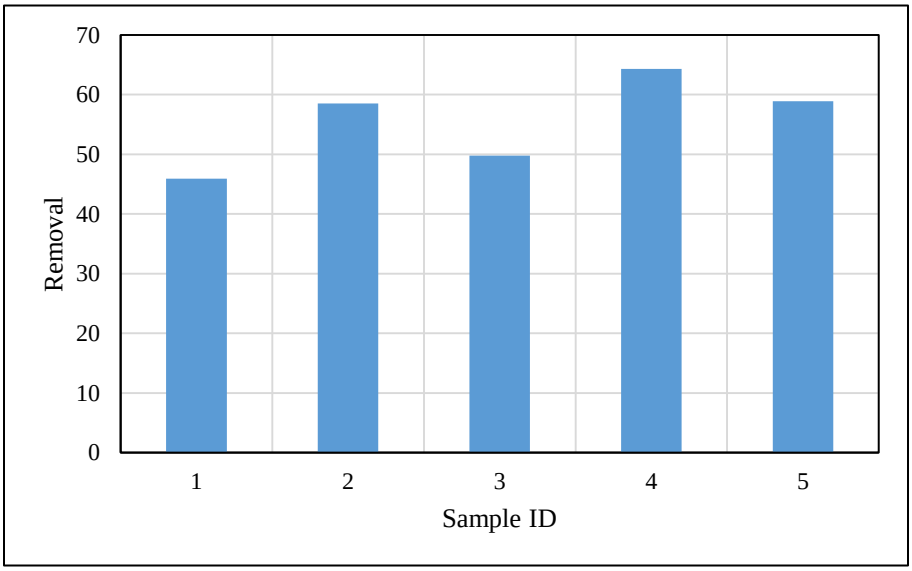


Figure 4.11:Effect of activation parameters on the removal efficiency of Pb (II)

4.1.3.5 Effect of Process Parameter on Surface Area of Prepared AC

The pours structure of the prepared AC was investigated by nitrogen adsorption-desorption isotherms. Nitrogen adsorption- desorption isotherms were carried out for only 3.0 samples which had the best removal of MB, Cd (II), and Pb (II) , namely sample 1, 4, and 5, the activation conditions of the investigated samples are shown in table (4.2). The influence of different activation conditions on the produces BET surface area for the prepared AC samples are represented in figure (4.12). The obtained results showed that BET surface area increased from around 715 m^2/g to 793 m^2/g when the activation temperature increased from 600 C to 700 C, which indicates that the increasing in activation temperature led to increase in the BET surface area due to the release of non-carbonaceous materials from the raw material, so more pores were formed. On the other hand, the BET surface area decreased from 793 m^2/g to 708 m^2/g at the same activation temperature (700 C) and time (2 hours) when the concentration of the activating agent increased from 30% to 50 %. This maybe because when the impregnation ratio increased the created pores were collapsed or combined together, so that the produced BET surface area decreased as discussed before in the adsorption of Cd(II) and Pb(II) section . These results are in completely agreement with the results of adsorption of heavy metals which explains the variation of metal removal. The obtained results are in good agreement with Girgis and El-Hendawy [77] who investigated the effect of temperature and impregnation on AC prepared from date pits with phosphoric acid. They observed that the surface area of prepared AC increased when the temperature increased from 300 to 700 C^o where maximum surface area was obtained. It was also reported that at 700 $C^{o,}$ the increase in the acid concentration from 30% to 40% and from

50% to 60% led to decrease in the surface area which was attributed to the formation of skin or insulating layer which covers AC particles and reduce the surface area. The effect of temperature and acid concentration on the surface area of AC prepared from grain sorghum with H_3PO_4 also studied by Diao et al [78]. The result of this study revealed that there is increase in surface area with increasing the temperature from 450 to 600 C^o, then slightly decrement at 700 C^o was noticed. They also found that the surface area of AC decreased when acid concentration increased from 35% to 50 %.

Based on the obtained results of MB removal, heavy metals removal and BET surface area, the best activation conditions were determined as 700 C activation temperature, 120 minutes activation time, and 30% concentration of activating agent. The sample prepared at these activation condition produced the maximum removal of MB and heavy metals as well as the highest surface area were sample. Table 4.3 summarizes the best activation conditions based on the investigation of various characterization.

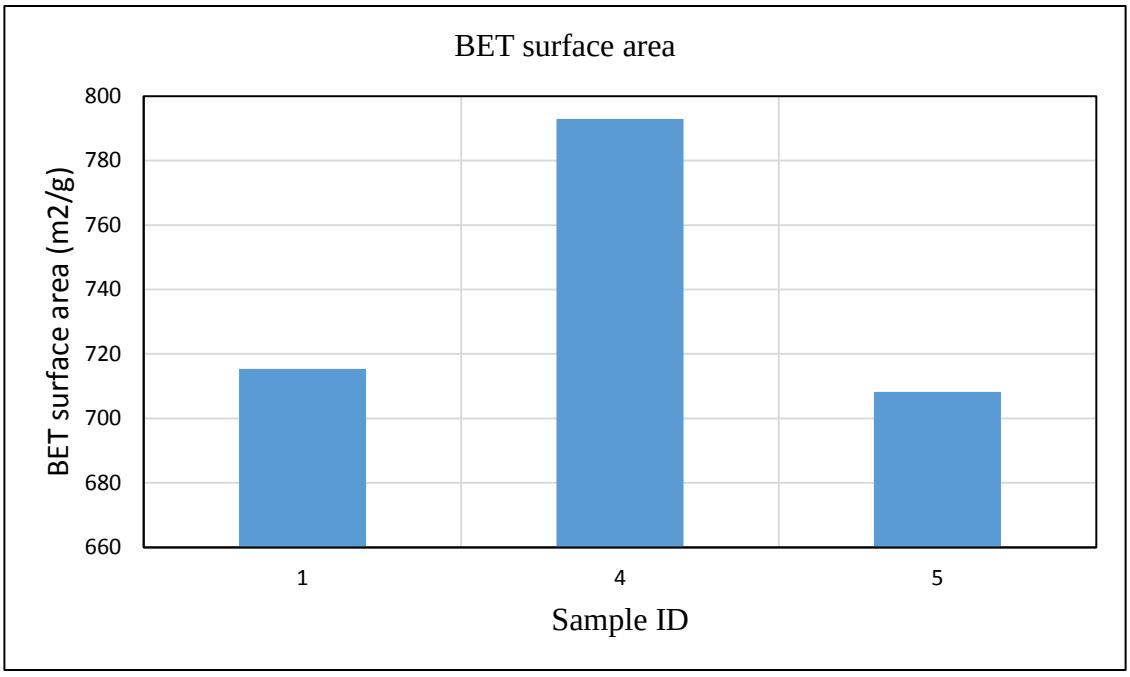


Figure 4.12:BET surface area for the prepared AC samples

Table 4.3: summary of the best activation condition based on different characterization

Activation Conditions			Yield (%)	MB R (%)	Cd(II) R (%)	Pb (II) R (%)	BET m^2/g	Density g/cm^3
Temp. C^o	Time hr.	Conc. (%)						
700	2.0	30	32	100	54.7	64	792.931	0.60

4.1.3.6 Characterization of AC

Different Characterization were conducted on the activated carbon samples prepared at best conditions, including SEM, XRD, FTIR, proximate analysis and ultimate analysis.

4.1.3.6.1 Proximate and ultimate Analysis

CHNS analyzer (2400 Series II CHNS/O Analyzer (PerkinElmer, CT, USA)) was used to carry out the elemental analysis for prepared AC. Table 4.4 shows elemental analysis of prepared AC. Comparing to the analysis of raw material (HOW) (Table 4.1), It was noticed that there are increase in carbon content and decrease in hydrogen nitrogen, and oxygen, which might resulted from carbonization process and release of non-carbonaceous material. Close findings were reported by Ahmad *et al.*[79], who prepared AC from pomegranate peel.

Table 4.4: Proximate and ultimate analysis of prepared AC

Proximate analysis		Ultimate analysis	
Property	Content (%)	Element	Content (%)
Moisture	11.11	C	58.82
Ash	11.80	H	3.3
Volatile	19	N	2.96
Fixed carbon	58.0872	S	0
		O	34.92

4.1.3.6.2 Surface Chemistry Characterization

Adsorption capacity of activated carbon depends not only on the porosity and surface area, but also affected by the surface chemistry, which depends on the chemical bond between carbon and heteroatoms including oxygen, hydrogen and nitrogen. Activated carbon basically consisting of carbon and contains varying amount of heteroatoms, which bounded to the carbon atom creating the surface functional groups as reported by Rodriguez-Reinoso [80]. All these functional groups influence the surface of AC, but oxygen functional groups are more strongly influence the properties of AC surface due to the high electronegativity of oxygen atoms, which particularly enhance the adsorption characteristics of AC in aqueous solutions as stated by Harry and March [81]. Detailed study of the significance of oxygen functional groups on the surface of AC was investigated by Boehm [82].

Fourier Transform Infrared (FTIR) spectroscopy technique was applied to determine the surface functional groups of raw materials and A.C samples using (Thermo Electron Corporation Nicolet Nexus 670 FT-IR Spectrometer). FTIR spectra of raw material (HOW) and AC sample were reported within 500 – 4000 cm^{-1} as shown in Figure 4.13. Almost the same functional groups were found in the raw materials and prepared AC, which indicates that the activation process only enhanced the porosity and little change of surface chemistry was observed. Similar notations was observed by El Hendawy *et al.*[83] , who prepared AC from cotton stalks with phosphoric acid. The spectra of raw material (HOW) and prepared AC as shown in the figure revealed presence of different functional groups, including Oxygen functional groups, amines, and unsaturated hydrocarbon. In case of raw material (HOW), the presence of hydroxyl with

high intensity broad peak was observed at 3447.This was also observed at 3448 cm^{-1} by A. El-Hendawy [84]. The sharp peaks at2895 and 2925 cm^{-1} and might due to the presence of symmetric and asymmetric C-H methylene and methyl group respectively. This was also observed at2864 cm^{-1} and 2924 cm^{-1} elsewhere [84]. The strong band at 1745 cm^{-1} is ascribed to the carbonyl ester group (C=O). This band was also observed at wave number of 1742 $cm^{-1}$and 1745 cm^{-1} by El-Hendawy *et al*. ,and El-Hendawy respectively [82 ,81]. The strong band at 1645 cm^{-1} might attributed to the presence of C=C alkane group. The medium band at 1416 cm^{-1} might ascribed to the presence of C-H bending of methylene group. The strong bands at around 1150 and 1080 cm^{-1} may attributed to the presence of C-O alcohol and ester starching group respectively. The strong band stretch C-H group was observed at low wave number (670) cm^{-1}.

In case of prepared AC, the main observed difference between the spectra of raw material (HOW) and prepared AC as shown in Figure 4.13 was the weak intensities of different waves of AC compared to the raw material. This might attributed to the effect of phosphoric acid impregnation and high carbonization temperature. During the activation process at high temperature, there is increase in volatile matter due to carbonization and aromatization, which break up and destruct the chemical bonds leading to weak intensities as reported by many researchers [81,82]. Sharp decrease in the band intensities of AC prepared from cotton stack was also observed by El-Hendawy *et al.*[63], who prepared AC from cotton stalks with H_3PO_4 at 700 C^o.

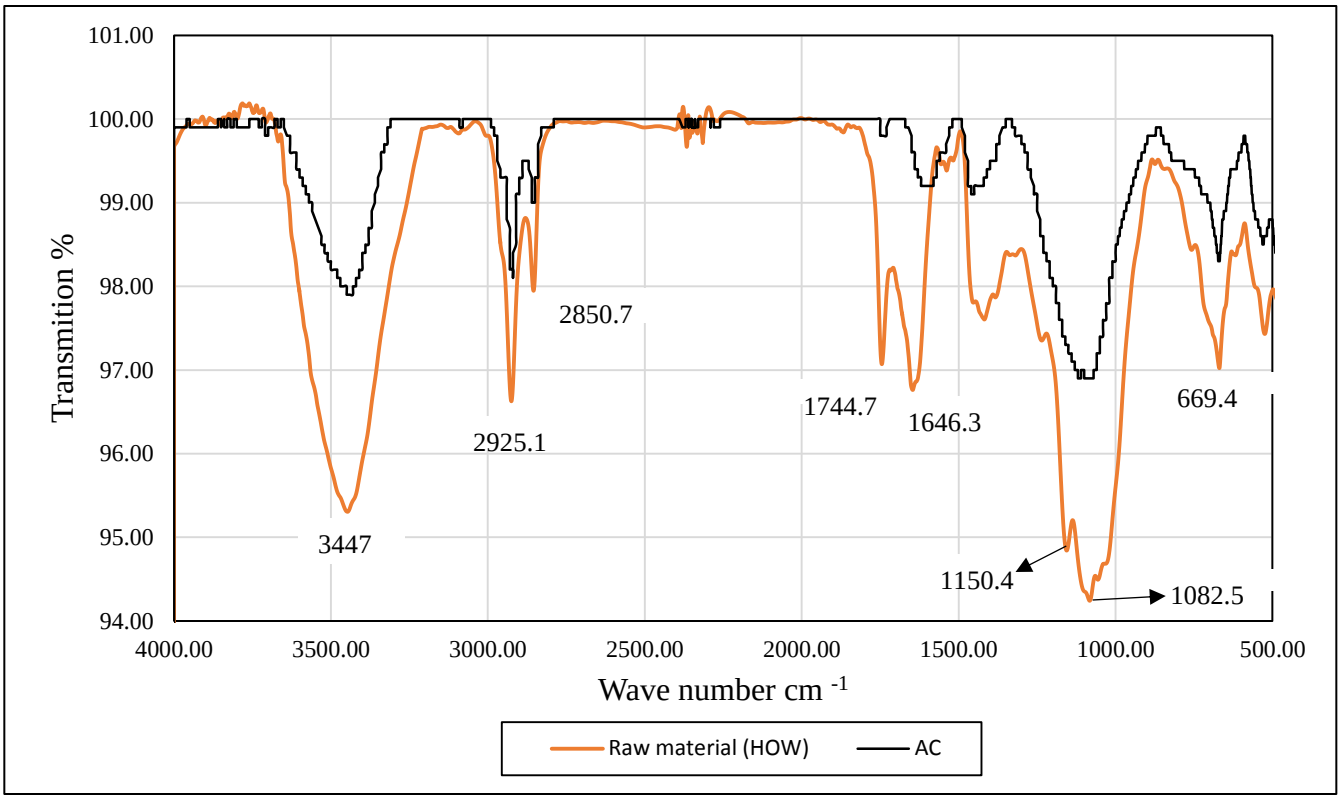


Figure 4.13:FTIR spectra of raw material (HOW) and prepared AC

The weak intensities of AC spectra due to the carbonization and aromatization was confirmed by the presence of strong band at 1745 cm^{-1} in raw material which was shifted to 1740 cm^{-1} and became very weak in AC. El-Headway [84], who prepared AC from date pits with 50% H_3PO_4 also noticed the appearance of band 1742 cm^{-1} in raw material and absence in prepared AC. In addition El-Hendawy *et al.*[63], observed the presence of band 1745 in raw material (cotton stalk) while it was absence in the prepared AC. In these previous studies the bands around 1745 cm^{-1} disappeared while it was very weak in this study. This is might because of the difference in the concentration of H_3PO_4. In this study the raw material was impregnated with 30% while 50% was used in the previous study [84]. Furthermore, It was noticed that the group C=C at 1646 cm^{-1} in raw material shifted to 1590 cm^{-1} and look weaker in AC. This might ascribed to the condensation of aromatic group during the activation process. Similar findings was also observed by El-Hendawy *et al.*[63], where the wave number shifted from 1600 cm^{-1} in raw material to 1575 cm^{-1} in AC. Moreover, the C-H group which was observed at 1416 cm^{-1} in the raw material shifted to 1450 in AC due to the formation of C=C because of carbonization and aromization. The strong bands at around 1150 and 1080 cm^{-1} in the spectra of AC may ascribed to linear and cyclic polyphosphate ester group P=O due to the treatment with phosphoric acid. This is consistent with the increase in content of phosphorus in the surface of AC compared to the raw material as shown in the result of SEM analysis. This is in good agreement with findings observed by many researchers [81,82,83]. Fernandez *et al.*[85], investigated the FTIR spectra of AC prepared from orange peel with 50 (wt. %) phosphoric acid. They observed the presence of P-O

functional group at 1070 cm^{-1} .Functional groups of raw material and prepared AC is summarized in Table 4.5 & Table 4.6 respectively.

Table 4.5: FTIR of Raw Material (HOW)

Peak wave length cm $^{-1}$	Functional group	
	type	Formula
564.6	alkanes	C–H
669.4	alkanes	C-H
1082.5	Ether	C-O
1150.4	Alcohol	C-O
1416.5	Aromatic	C-H
1646.3	alkenes	C=C
1744.7	Carbonyl(Ester)	C=O
2850.7	alkanes	C-H
2925.1	alkanes	C-H
3447	Carboxyl	C-OH

Table 4.6: FTIR of prepared AC

Peak wave length cm -1	Functional group	
	type	Formula
481.7	alkanes	C–H
670.1	alkanes	C-H
1079.8	polyphosphate-ester	P-O
1150	polyphosphate-ester	P-O
1450	Aromatic	C=C
1590.5	Aromatic	C-C
1740	Carbonyl(Ester)	C=O
2850.7	alkanes	C-H
2923.5	alkanes	C-H
3444.5	Carboxyl	C-OH

4.1.3.6.3 Microscopy

Scanning Electron microscope (SEM) was used to examine surface topology, including the sizes and shapes of pores on the surface of raw material (HOW) and AC. (EDS) technique was employed to investigate the elemental composition of sample surface of raw material (HOW) and prepared AC. This analysis was conducted to examine the effect of activation process in terms of porosity development and surface chemical composition change since these two factors plays key role in adsorption characteristics of AC.

Table 4.7 & Table 4.8 shows the elemental composition of the surface of raw material (HOW) and prepared AC. In each sample, the elemental analysis of 3 local spots were investigated and average value was considered as illustrated in the tables. The major components of both raw material (HOW) and prepared AC were carbon, oxygen, and small amount of calcium, potassium, phosphor and chloride. The results revealed that during the activation process, non-carbonaceous materials were removed. This was consistent with the increase in carbon content from around 64.4 % in raw material to 82.4 % in activated carbon and the absence or sharp decrement in the other metals in AC elemental analysis. Moreover, phosphorus content increased from around 0.30% in raw material to around 4.6 % in AC due to the impregnation with phosphoric acid. As illustrated in Table 4.8, major component of AC are C, O and P indicating that the surface is rich in oxygen and phosphor functional groups. This is consistent with FTIR analysis of AC discussed in section (4.1.3.6.3).

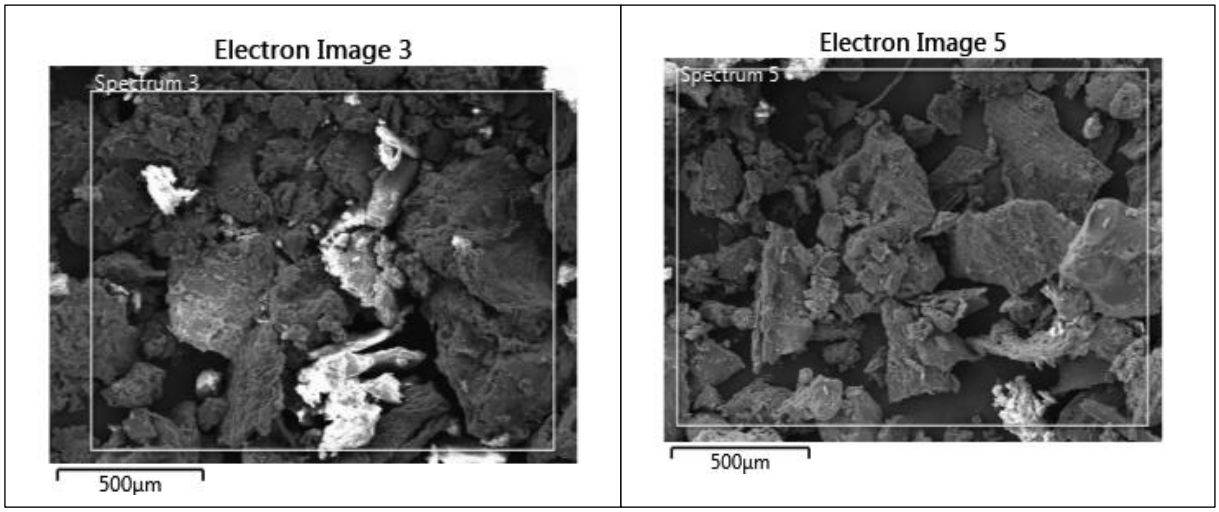
The SEM micrographs of raw material (HOW) and the prepared AC are illustrated in Figure 4.14 & Figure 4.15. Comparing the micrographs before and after activation, it was clearly observed the formation of different pores due to activation process. The micrographs also shows the heterogeneity surface of AC and irregular distribution of pores.

Local spot	C (%)	O (%)	Ca (%)	K (%)	Cl (%)	P (%)
Spot1	64.6	32.7	1.8	0.6	0.3	0.2
Spot2	63.1	33.2	2.2	0.7	0.3	0.6
Spot3	65.5	32	1.3	0.5	0.2	0.2
Max	65.5	33.2	2.2	0.7	0.3	0.6
Min	63.1	32	1.3	0.5	0.2	0.2
Average	64.4	32.6333	1.76667	0.6	0.26667	0.33333

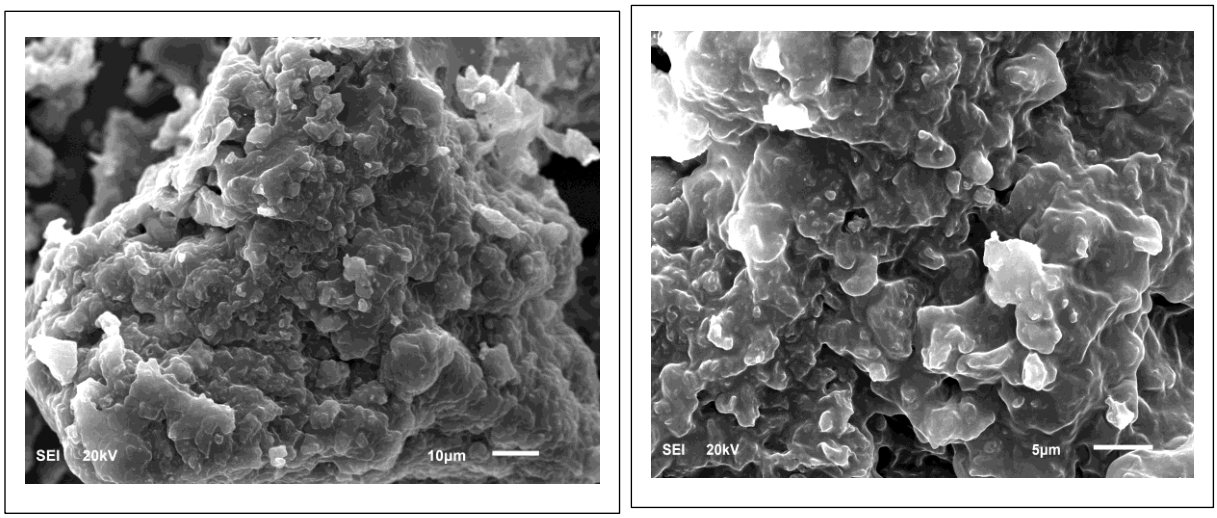
Table 4.7:Localized spot elemental analysis of raw materials (HOW)

Table 4.8:Localized spot elemental analysis of AC

Local spot	C (%)	O (%)	P (%)	Ca (%)
Spot1	82.7	12	4.7	0.6
Spot2	81.6	12.4	4.4	0.5
Spot3	83	11.8	4.7	0.5
Max	83	12.4	4.7	0.6
Min	81.6	11.8	4.4	0.5
Average	82.4333	12.0667	4.6	0.53333

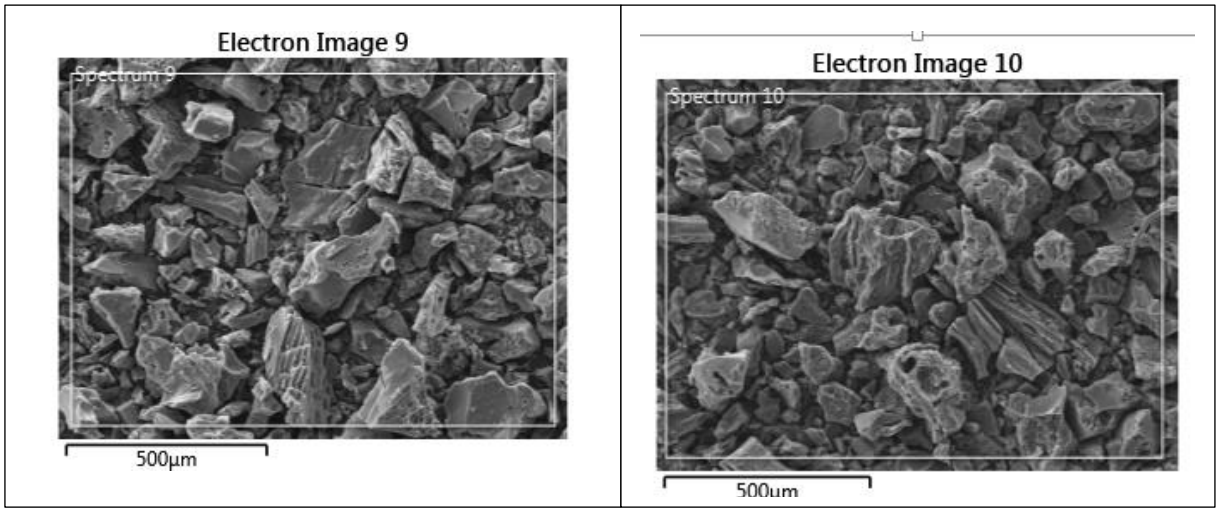


(a) (b)

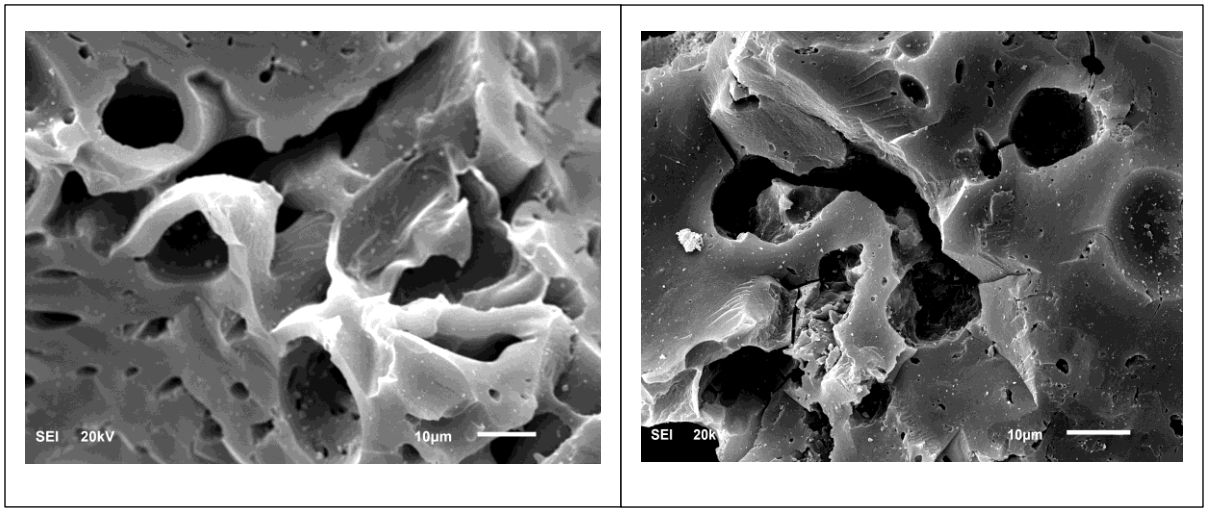


(c) (d)

Figure 4.14:SEM micrographs of raw material (HOW) (a-b) law resolution , (c-d) high resolution



(a) (b)



(c) (d)

Figure 4.15: SEM micrographs of prepared AC (a-b) law resolution, (c-d) high resolution

4.1.3.6.4 X-ray diffraction spectroscopy

According to Franklin [86], there are two types of carbon in terms of graphitizing ability, graphitizing and non-graphitizing carbon. Good porous characteristics of activated carbon can be developed from non-graphitizing carbon because it is strong, amorphous and has strong crosslinking between the adjacent crystallites.

Crystalline structures of raw material (HOW) and AC were examined by X-ray diffraction technique (XRD), where (Ultima IV) X-ray diffractometer was employed for this purpose. Scan run was conducted in the range angle from 10^o to 80^o, with a step size of 0.02^o/s. The patterns of XRD of raw material and prepared AC are shown in Figure 4.16 & Figure 4.17 respectively. In both patterns, no sharp peaks was observed, the broad peaks indicates that the structure is amorphous and non-graphitizing therefore good porous structure can be developed [87]. In raw material (HOW) the broad peak at $2\theta = 23^o$ might ascribed to the typical silica characteristics. This peak disappeared in the spectra of AC, which can be attributed to ash removal as a result of heat and acid treatment during activation process. Similar findings observed by Liou [71], who prepared AC from sugar cane bagasse with phosphoric acid.. As shown in Figure 4.17, the presence of broad peaks at $2\theta \approx 26^o$ and $\approx 43^o$ in the XRD of AC indicates that better alignment of crystalline structure was formed .This was also reported by Tongpoothorn *et al.* [88] who prepared AC from Jatropha curcas fruit shell. In addition, of these two peaks ($2\theta \approx 26^o$ and $\approx 43^o$) might ascribed to the presence of particular graphite and sodalite or mullite respectively. Similar peaks was observed by Salehin *et al*. [89],where XRD of AC from residual oily fly ash was investigated .

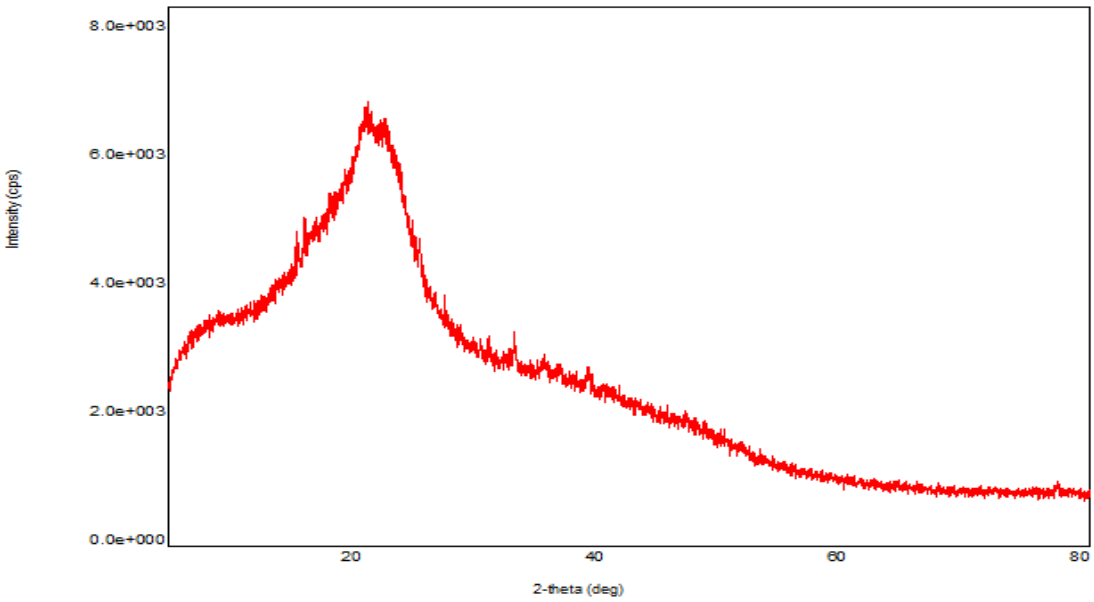


Figure 4.16: XRD of Raw material

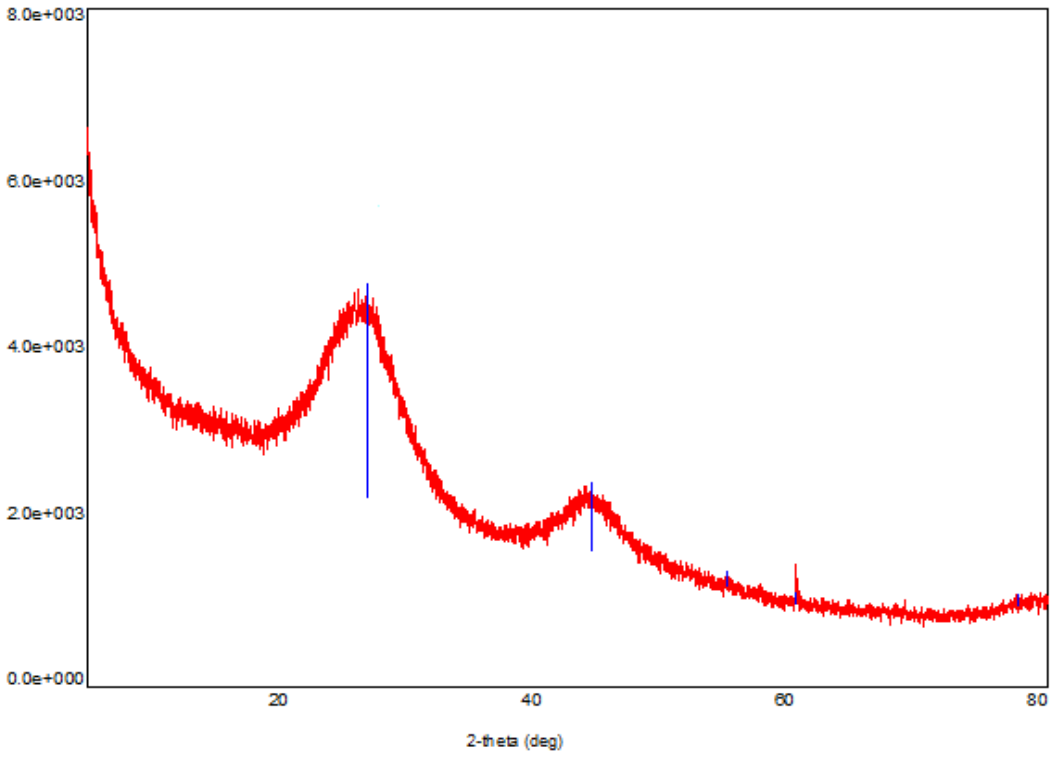


Figure 4.17: XRD of prepared AC

4.2 Single adsorption of Cd (II) and Pb (II) on the Prepared AC

In this section the potentiality of the prepared activated carbon for the removal of heavy metals from synthetic industrial wastewater in single aqueous medium will be investigated.

4.2.1 Effect of operational parameters

The effect of different operational parameters on the adsorption capacity of Cd (II) & Pb (II) on the prepared samples were examined including pH, contact time, adsorbent dosage and metal initial concentration in terms of single as well as competitive adsorption.

4.2.1.1 Effect of pH

PH of the solution is one of the most significant parameters that effect the removal heavy metals from aqueous solutions because it controls the solubility of metal ions in addition to ionization degree of metal ions during adsorption process. Furthermore the surface charge of adsorbent is highly pH dependent, this was also reported by Bakather who studied the removal of lead from synthetic solution using carbon nanotube [90].

AC prepared at the best conditions were investigated for the removal of Cd (II) and Pb (II) at pH range from 3.0 to 7.0 (3.0, 4.0, 5.0, 5.50, 6.0, and 7.0).These values were investigated based on the fact that at pH higher than 7.0 precipitation of metal ions occurs. This was also reported by Li et al [91] who studied the adsorption and desorption of lead from solution, so to evaluate the adsorption capacity by AC only and not by precipitation, these values were selected. Batch experiments were conducted at initial

metal concentration of 100 mg/l, 50 mg adsorbent dosage, 3.0 hours contact time, 50 ml solution volume, and 200 rpm shaking speed. The pH variation effect on the efficiency removal of Cd (II) and Pb(II) on prepared AC are presented in Figure 4.18 & Figure 4.19 respectively .The obtained results showed that the increase in pH value enhanced the efficiency removal for both metals Cd (II) and Pb(II). When the pH increased from 3.0 to 7.0 the removal efficiency enhanced from 26.5 % to 38 % and from 50% to 85 % for cadmium and lead respectively. At lower pH values there is strong competition between hydrogen ions and metal ions for AC surface sites which resulted in lower removal but when the pH increases the competition decreases due to the decrease in positive charge H^+ and increase of OH^- [90,76]. Taty-Costodes *et al.* [92] investigated the effect of pH on the removal efficiency of cadmium and lead by sawdust, where similar notations were reported.

It was also observed that, for the removal of Cd (II) and Pb (II), gradually increasing in the removal efficiency when pH value increased from 3.0 to 5.0, and negligible change from 5.0 to 6.0. However, dramatically increasing of the removal efficiency was observed when the pH increased from 6.0 to 7.0. This may resulted from adsorption as well as precipitation of the metal ions as hydroxide at pH 7.0. This was confirmed by the variation of metal concentration with respect to pH values as shown in Figure 4.20 & Figure 4.21, where precipitation was clearly observed. Therefore, Further studies were conducted at pH =5.0 to avoid any removal due to precipitation. Optimum pH of 5.0 also observed by many researchers [92 ,87] who studied the removal of cadmium and lead single solution on AC prepared from apricot stone and oil fly ash respectively.

The removal efficiency of Pb (II) was higher at the same pH values, which means Pb ions more preferred than Cd ions for prepared AC. This may attributed to the different in metal properties especially the electronegativity, where lead has much higher electronegativity (2.33) than cadmium (1.69) because the higher electronegativity the stronger attached to the AC surface.

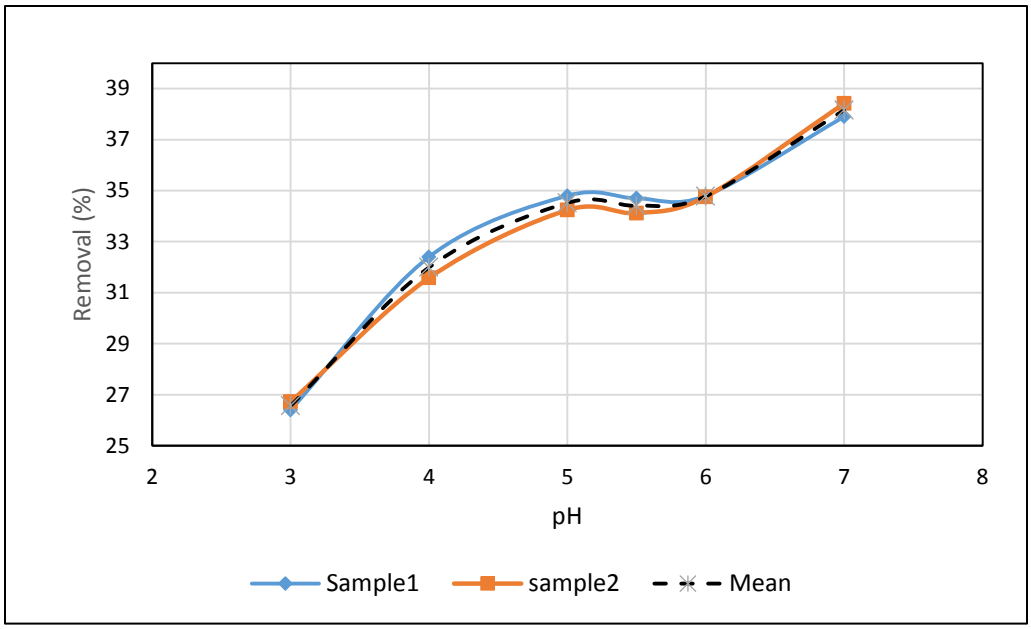


Figure 4.18:Effect of pH on Cd (II) Removal Efficiency

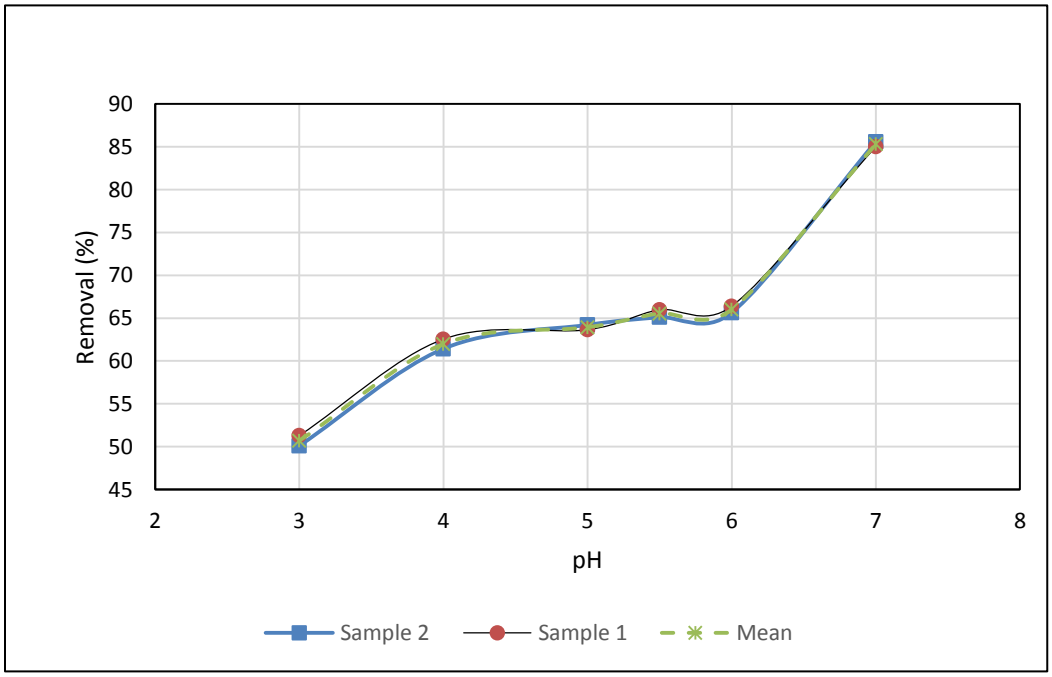


Figure 4.19:Effect of pH on Pb (II) Removal Efficiency

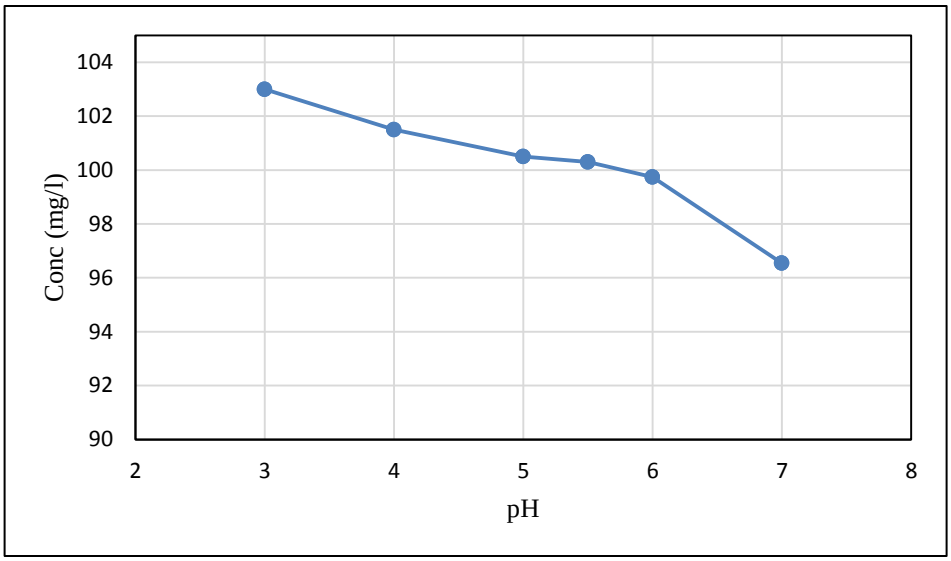


Figure 4.20:Concentration variation of blank samples of Cd (II)

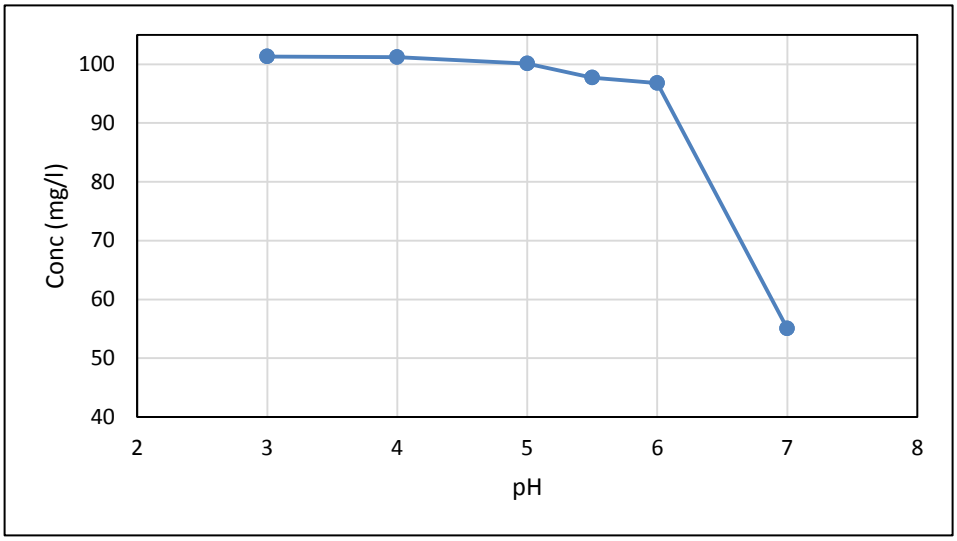


Figure 4.21:Concentration variation of blank samples of Pb (II)

4.2.1.2 Effect of Contact time

To investigate the effect of contact time on the removal efficiency of Cd (II) and Pb (II) in single mode by prepared AC, batch experiments were performed at different times in range of 5.0- 480 minutes under the following constant conditions; pH =5.0, initial metal concentration of 100 mg/l, adsorbent dosage 50 mg /50 ml of solution.

Figure 4.22 &Figure 4.23 shows the variation of removal efficiency of Cd (II) and Pb (II) with respect to time in single metal solutions. The removal efficiency of both metals increased dramatically from 5.0 to 30 minutes, then gradually increased from 30 to 120 minutes. After 120 minutes almost constant removal observed, where the equilibrium occurred at 120 minutes for both metals. The fast adsorption within the first 30 minutes may related to the high availability of surface area and active sites on the surface of AC, the metal ions adsorbed quickly in the more active sites .Once these sites are filled, adsorption become more difficult until saturation is reached. The equilibrium time was obtained at 120 minutes. , where the adsorbed molecules of metal ions equals the leaving ones. The maximum removal at the equilibrium was 34.5 % and 63 % for Cd (II) and Pb (II) respectively. Similar findings was found where equilibrium time of 120 minutes for the removal of cadmium and lead was reported by many researchers [93,94]. They studied the removal of lead and cadmium by treated pinus pinaster bark and activated carbon from different agricultural waste respectively. Further adsorption experiments were carried out using 180 minutes as contact time to emphasize that equilibrium is reached. Taty-Costodes *et al.*[92], studied the effect of contact time on the removal of cadmium and lead. They found that equilibrium time was reached in 20 minutes, however

contact time of 120 minutes were maintained for all following experiments to make sure that equilibrium is reached.

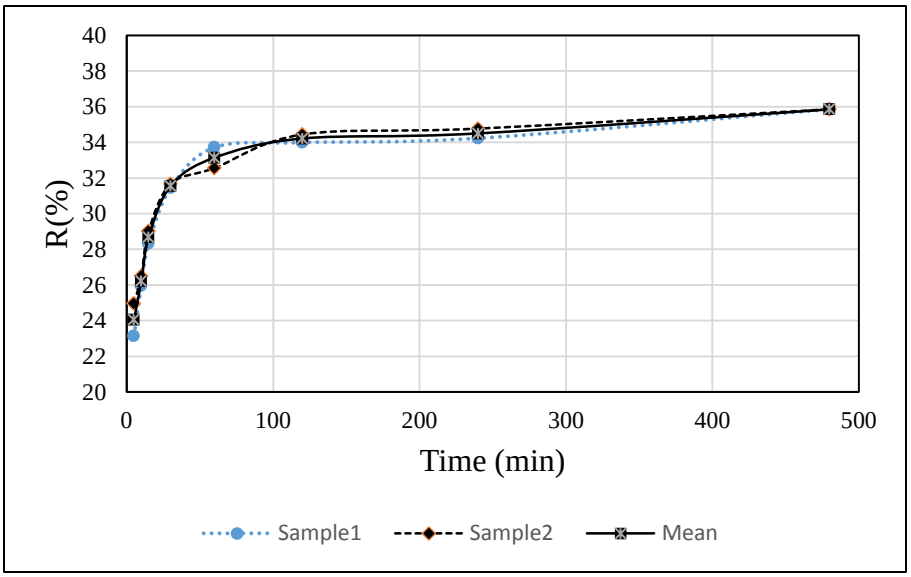


Figure 4.22: Effect of contact time on Cd (II) efficiency removal in single mode

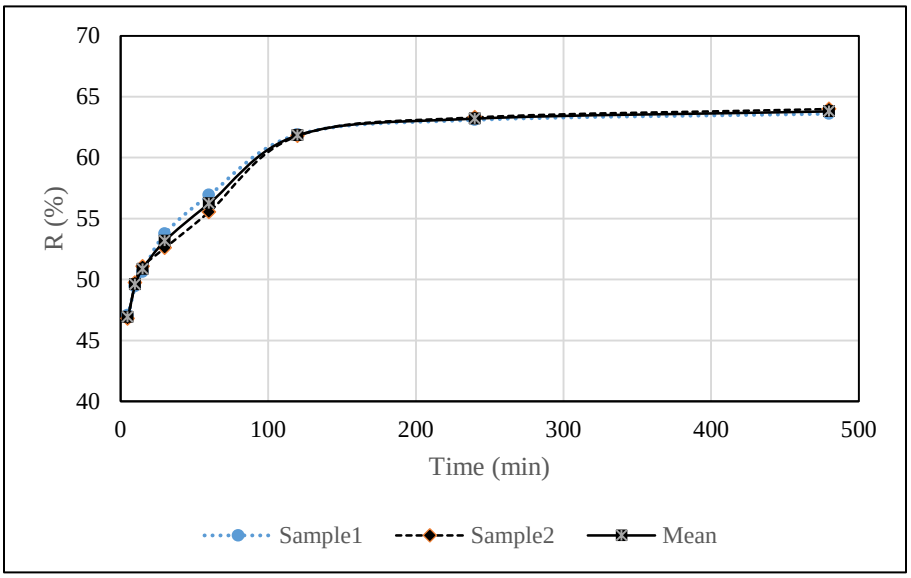


Figure 4.23: Effect of contact time on Pb (II) efficiency removal in single mode

4.2.1.3 Effect of Initial concentration

To investigate the effect of initial concentration on the removal efficiency of Cd (II) and Pb (II) in single mode by prepared AC, batch experiments were performed at different initial concentrations in range of (25- 300) ;(25, 50,100,200, and 300) mg/l; contact time 180 minutes; pH =5.0, and adsorbent dosage 50 mg /50 ml of solution.

The effect of initial concentration on the removal efficiency of cadmium and lead in single system is presented in Figure 4.24, & Figure 4.26 for cadmium, and lead respectively. The result revealed that when initial concentration increased from 25 mg/l to 300 mg/l, the removal efficiency decreased from 72 % to 20 % and from 98 % to 30 % for cadmium and lead respectively. The removal efficiency decreased gradually when the initial concentration increased from 25 to 150 mg/l for both metals, further increase in initial concentration led to small variation in metal removal. This can be interpreter as that, AC carbon surface contains definite number of high energy sites, at low concentrations the adsorption occurs at these high energy sites, when the concentration increases, these sites become saturated and the metal ions adsorbed on low energy sites where energy removal decreased. This was stated by A. Seco *et al* [93] who studied the effect of initial concentration on metal removal by granular AC.

On the other hand the adsorption capacity increased when increased the metal ions for adsorption capacity of both metals as shown in Figure 4.25 & Figure 4.27, the adsorption capacity increased from 18 mg/g to 56 mg/g, and from 24.5 mg/g to 90 mg/g when the initial concentration increased from 25 to 300 mg/g for cadmium and lead respectively. This may because the increase in initial concentration led to increase the

driving force which in turn overcome mass transfer between solid and liquid face. Moreover, the increase of metal concentration led to increase the interaction between the AC and metal ions. This was also reported by Taty-Costodes et *al*. [92] who studied the removal of cadmium and lead onto sawdust and Thajeel *et al*. [97] who used activated carbon from rice husk for lead removal.

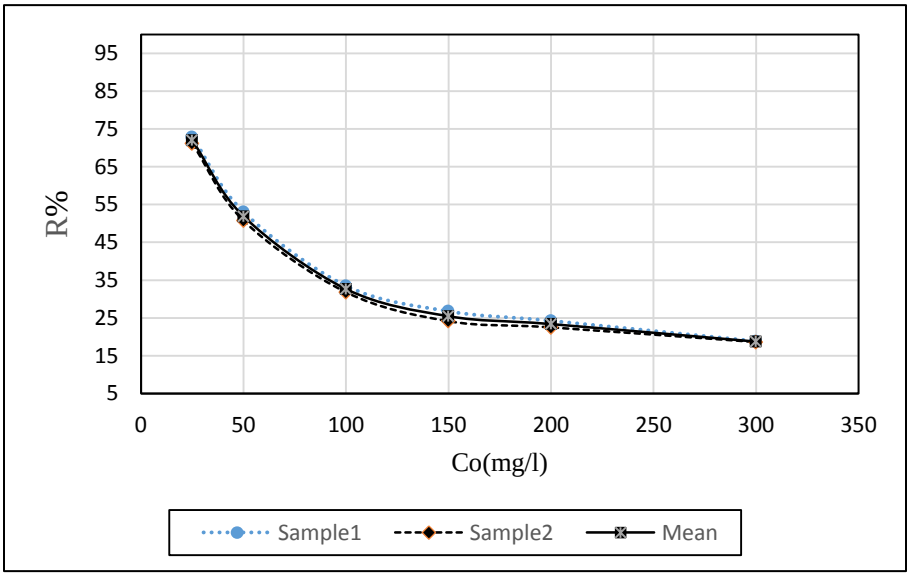


Figure 4.24:Effect of initial concentration on Cd (II) efficiency removal in single mode

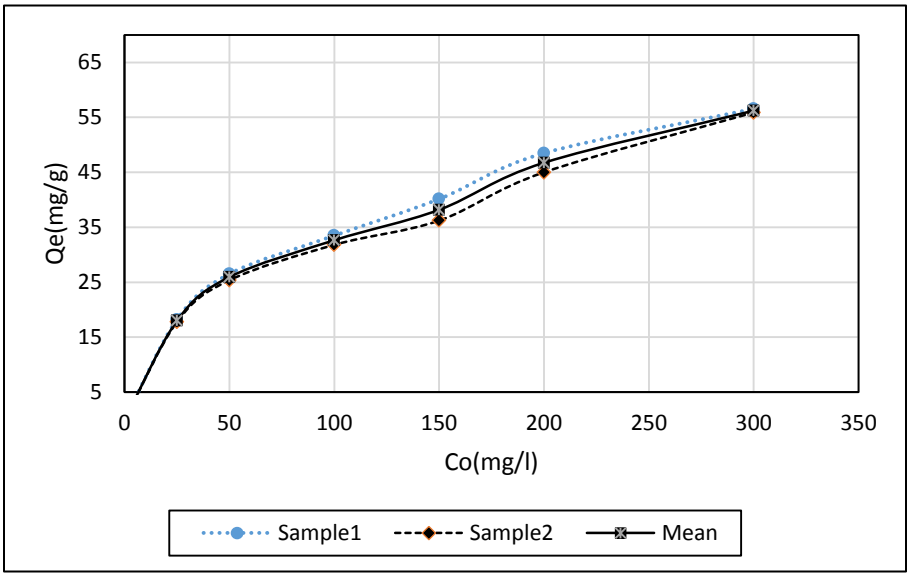


Figure 4.25:Effect of initial concentration of Cd (II) on AC adsorption capacity in single mode

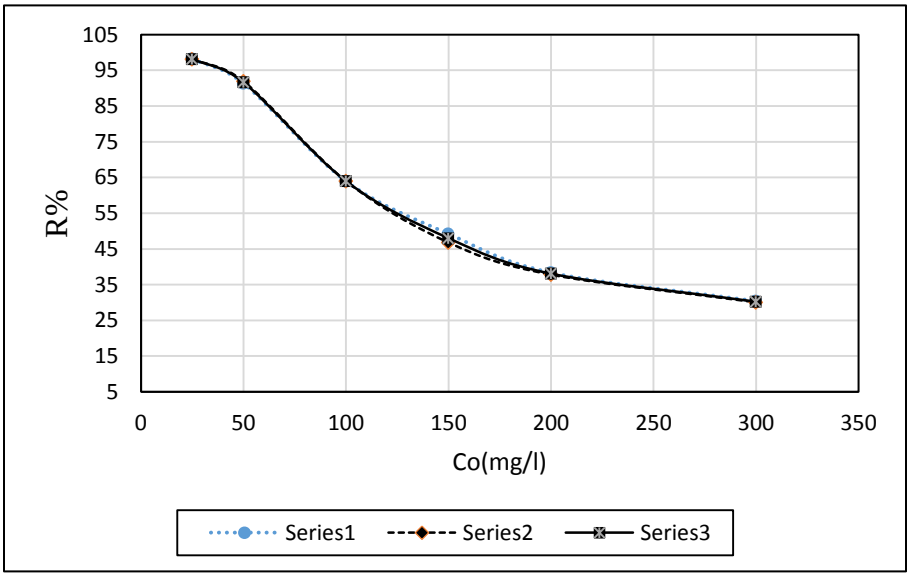


Figure 4.26: Effect of initial concentration on Pb (II) efficiency removal in single mode

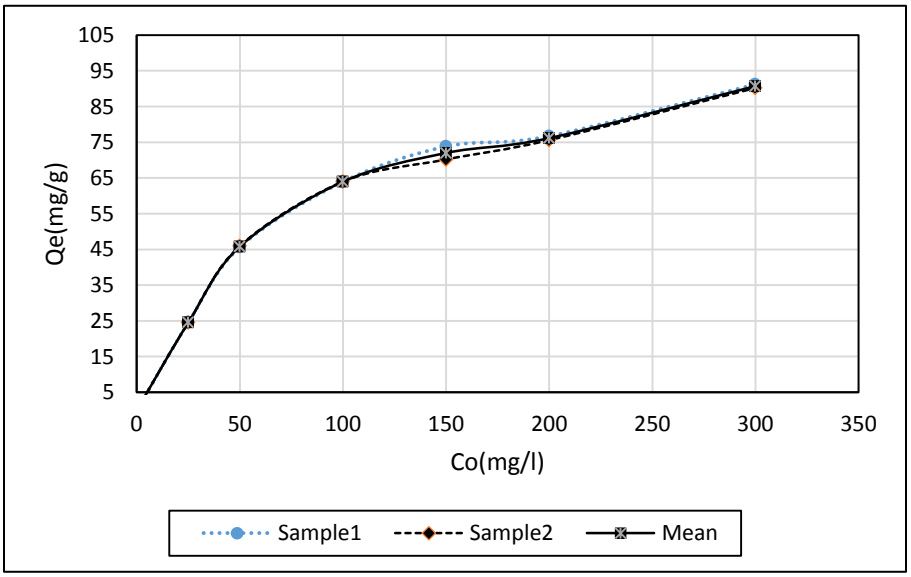


Figure 4.27: Effect of initial concentration of Pb (II) on AC adsorption capacity in single mode

4.2.1.4 Effect of Adsorbent dosage

To investigate the effect of AC dosage on the removal efficiency of Cd (II) and Pb (II) in single mode by prepared AC, batch experiments were performed with different AC dosage from 25 to 300 mg (25, 50, 100, 200, and 300), mg /50 ml at initial concentrations of 100 mg/l, contact time 180 minutes; pH =5.0.

Figure 4.28 & Figure 4.29 shows the effect of AC dosage on the removal efficiency of cadmium and lead respectively in single adsorption mode. The result revealed the removal efficiency of both metals increased gradually by increasing the AC dosage until specific value, where further increment of AC led to insignificant increasing in the removal efficiency. For cadmium removal (Figure 4.28), the increase in AC dosage from 25 to 200 mg/g the removal increased from 21 to 78 %, enhanced the removal by 60 %, however, further increasing in AC to 300 mg the removal efficiency increased to 85 % ,enhanced by only about 7 %. Similarly as shown in Figure 4.29 ,it was observed that when AC increased from 25 to 200 mg the removal of Pb (II) increased from 36 to 94 %, increased with about 60%, but with further increasing in AC to 300 mg , the removal efficiency increased to 98 %, increased by about 4 % only. This is because by increasing the adsorbent dosage with constant metal concentration, the surface area as well as adsorption sites increases which enhances the removal efficiency, but with further increasing in AC, no significant increase in the removal which may because the equilibrium between the residual concentration of metal ions in the solution and surface metal ions concentration is reached as reported by Srivastava *et al.*[98] , who studied the adsorption behavior of toxic metals by AC prepared from coconut.

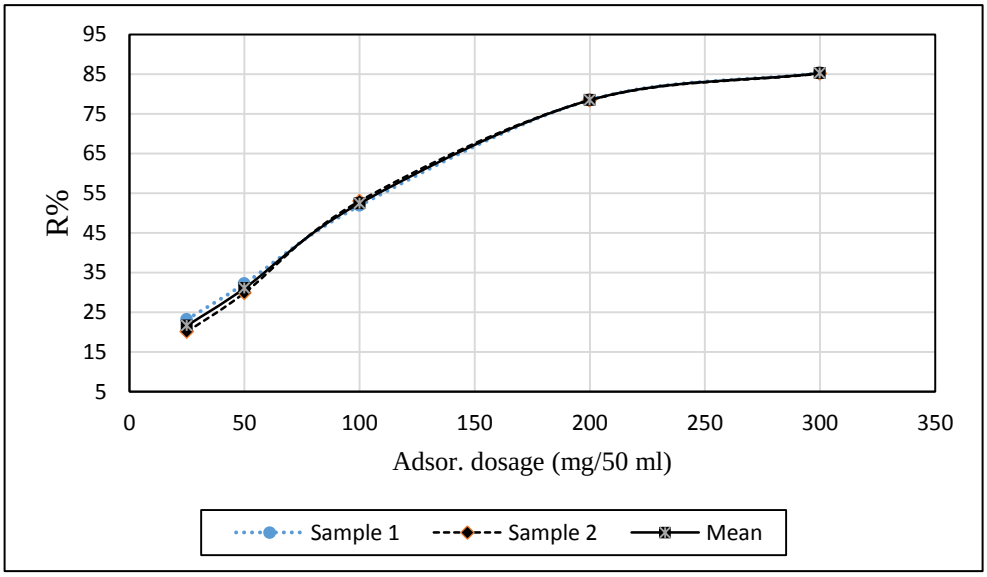


Figure 4.28: Effect of AC dosage on removal efficiency of Cd (II)

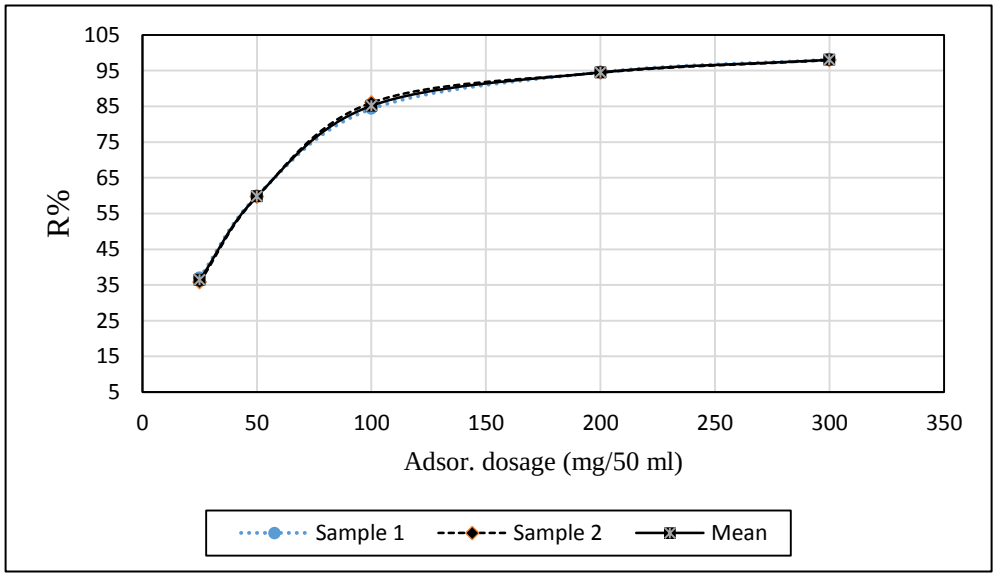


Figure 4.29: Effect of AC dosage on removal efficiency of Pb (II)

On the other hand, the increase in AC dosage led to decrease in Adsorption capacity of both metals as shown in Figure 4.30 & Figure 4.31 , where adsorption capacity decreased from 43 to 14 %, and from 72 to 16 mg/g when AC dosage increased from 25 to 300, for Cd (II) and Pb (II) respectively. For constant metal concentration, at lower adsorbent dosage all adsorption sites are become saturated so the adsorption per gram is high, with increase the AC dosage the unsaturated adsorption sites increases, thereby the adsorption per gram decreases [99]. Moreover, the decrease of adsorption capacity might because of the overlapping of the adsorption sites as a result of overcrowding of AC particles as stated by Onundi *et al*.[100], who used AC from palm shell for the removal of lead and nickel from synthetic solutions. Similar findings observed by [101] who investigated the removal of lead by bael tree leaf powder.

The highest removal efficiencies of cadmium and lead were found to be 85 % and 98 %, where AC dosage was 300 mg respectively. Whereas maximum adsorption capacities were reported as 43 and 72 mg/g with 25 mg of AC for cadmium and lead respectively.

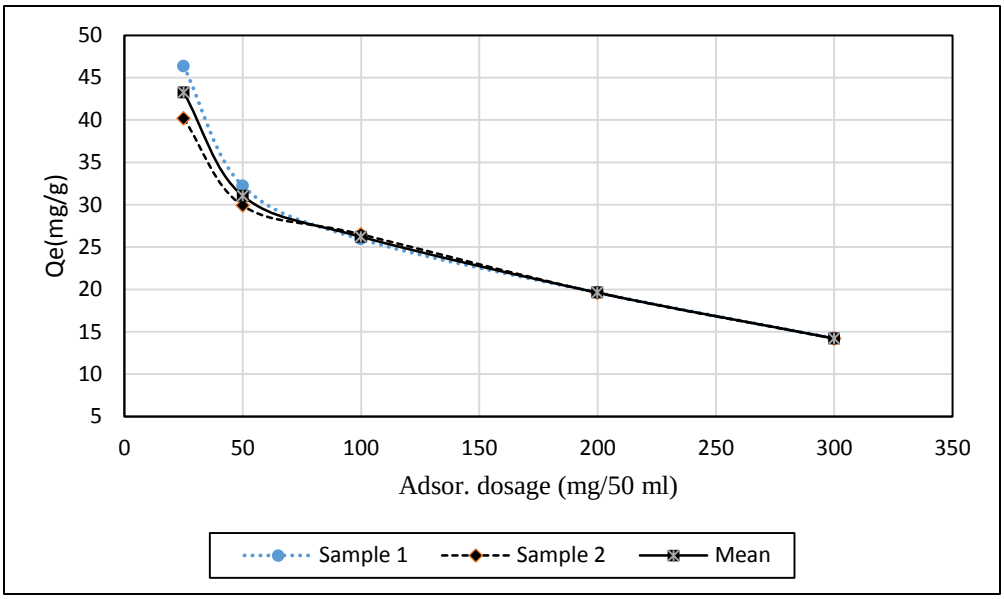


Figure 4.30:Effect of AC dosage on adsorption capacity of Cd (II)

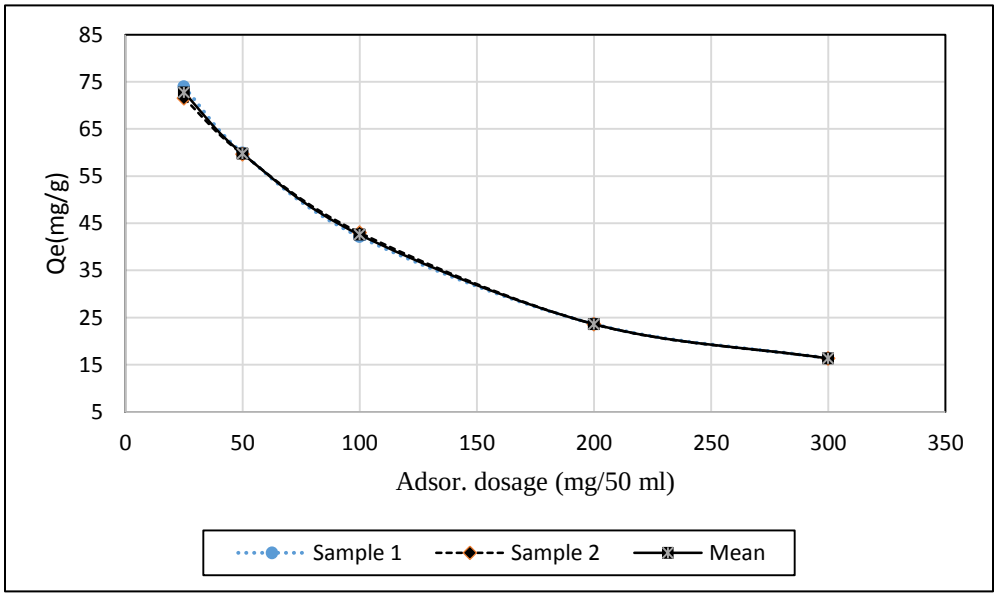


Figure 4.31: Effect of AC dosage on adsorption capacity of Pb (II)

4.2.2 Adsorption Equilibrium Isotherms

The obtained experimental data for cadmium and lead adsorption on prepared AC from household organic waste was fitted to isotherm models of Langmuir and Freundlich.

4.2.2.1 Adsorption Equilibrium Isotherms for Cadmium in single metal adsorption

The linear form of Langmuir adsorption isotherm (Equation (4.1)) was employed to plot the relation between the concentrations of metal in solid phase (qe) and the concentration of metal in liquid phase Ce at different initial concentrations of cadmium.

$$(Ce/qe) = \frac{1}{Kl} + \frac{al}{Kl} * Ce \qquad (4.1)$$

Figure 4.32 shows the Longmuir adsorption isotherm of cadmium on the prepared AC, where good fitting was observed with correlation coefficient of 0.9488. The parameters of the model were calculated and summarized in Table 4.9 below, where maximum adsorption capacity Q_o was found to be around 61mg/g.

The obtained data of adsorption capacity of cadmium at different concentration was also fitted to Freundlich isotherm using Freundlich formula (4.2) as shown in Figure 4.33. The results indicated good fitting and better than Langmuir where R^2 was found to be 0.978. The affinity in Freundlich isotherm is non-uniform over the surface of the adsorbent and each site on the adsorbent surface has different affinity which means adsorption of cadmium occurs as multilayers on heterogeneous surface of AC. Similar results reported by Mohan and Kumar [102] who studied the removal of cadmium by AC from bagasse. The Isotherm parameters was calculated and summarized in Table 4.9, the value of n (n=3.24) indicates good adsorption characteristics. According to Aksu and

Kutsal [103] who studied the removal of lead from waste water, the adsorption characteristics based on n values classified to three types; good for n values from 2-10, relatively good for n between 1.0 and 2.0 , and poor for n values less than one.

$$\log q = \log K + \frac{1}{n} \log C \qquad (4.2)$$

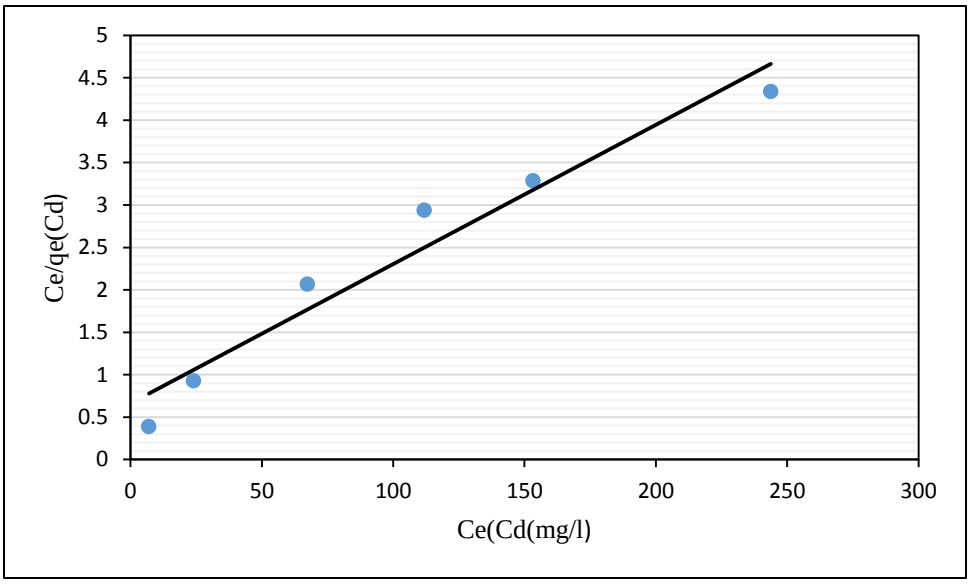


Figure 4.32:Langmuir isotherm of AC for cadmium adsorption capacity

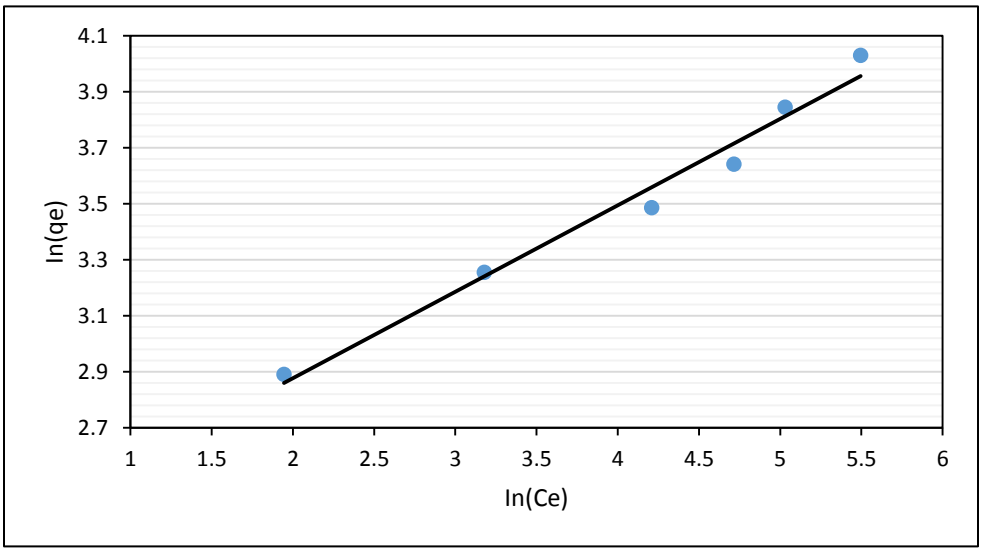


Figure 4.33:Freundlich isotherm of AC for cadmium adsorption capacity

4.2.2.2 Adsorption Equilibrium Isotherms for Lead in single metal adsorption

The experimental data of lead adsorption also fitted to Langmuir and Freundlich isotherms as shown in Figure 4.34 & Figure 4.35. The isotherms parameters were summarized in Table 4.9. It was observed that both isotherms were good fitted to the experimental results, but Freundlich isotherm was better fitted with higher correlation coefficient 0.987, indicating that adsorption of lead occurs as multilayers due to the heterogeneity of AC adsorption sites. Similar to cadmium adsorption characteristics, the value of n (n=3.30) indicates good adsorption. The maximum adsorption capacity Q_o was found to be 90 mg/g.

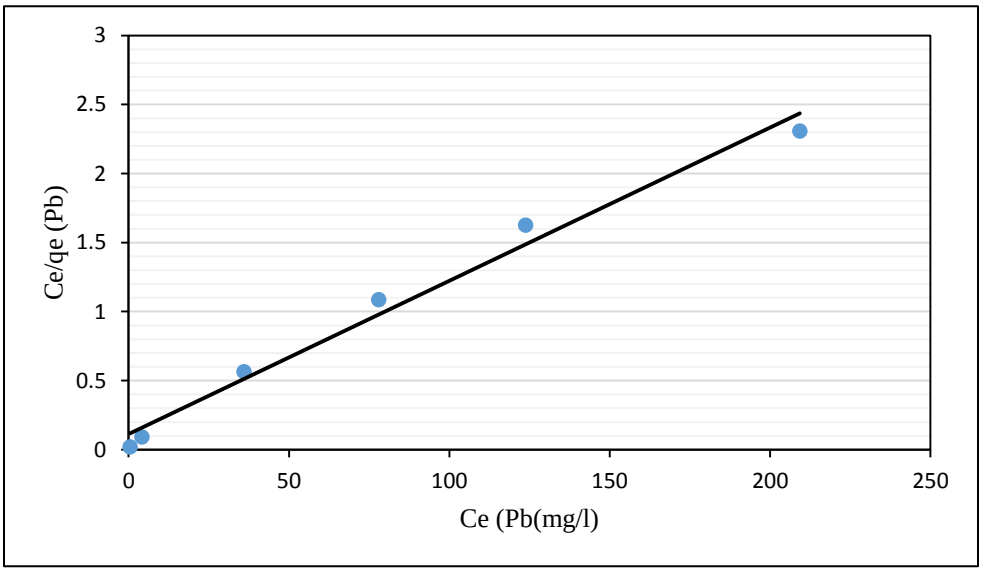


Figure 4.34:Langmuir isotherm of AC for lead adsorption capacity

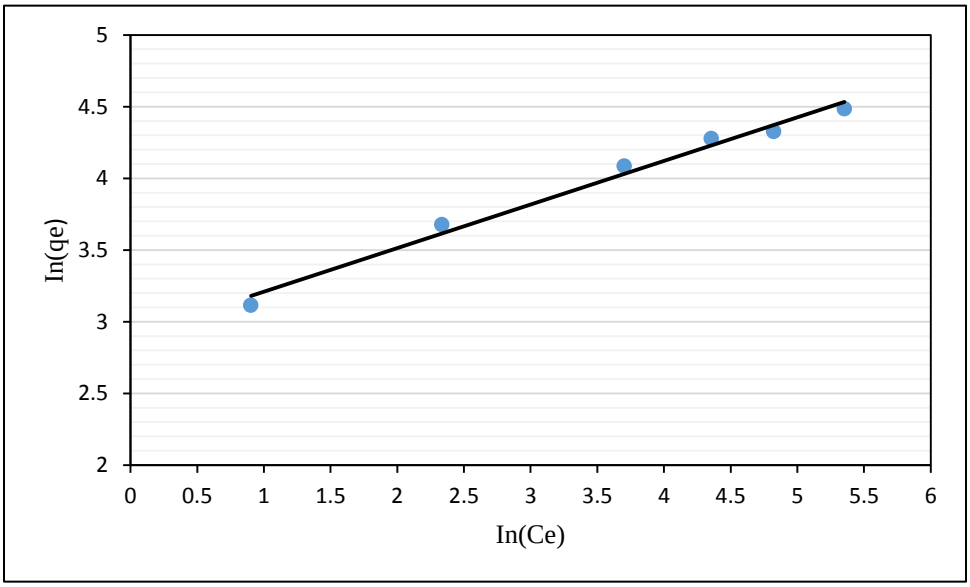


Figure 4.35:Freundlich isotherm of AC for lead adsorption capacity

Table 4.9:Isotherm Parameters of Langmuir & Freundlich of Cd (II) and Pb (II) in single adsorption

Isotherm parameter	Cd (II)	Pb (II)
Langmuir		
K_L(L/g)	1.520918	8.893532
a_L(L/mg)	0.024951	0.098735
Q_o (mg/g)	60.90591	90.06228
R^2	0.9488	0.984
Freundlich		
K_f (mg/g)	9.587417	19.18117
n	3.24	3.30
R^2	0.978	0.9870

4.2.3 Adsorption Kinetic Models

It is very important to study the adsorption efficiency which can be determined by kinetic models. They explain the adsorption mechanism whether it is chemical reaction or mass transfer. The experimental data was fitted to pseudo-first-order and pseudo-second-order kinetic models.

4.2.3.1 Adsorption Kinetic Models for Cadmium in single metal adsorption

The pseudo-first-order model was fitted to the experimental data of cadmium in single solution using the following formula

$$Log(qe - qt) = Log(qe) - \frac{K_1}{2.303} * t \qquad (4.3)$$

Where qe is equilibrium adsorption capacity (mg/g), q_t (mg/g) adsorption capacity at time t (min), and K_1 (1/min) is pseudo-first-order constant rate.

Figure 4.36 show pseudo-first-order plot for cadmium adsorption, where the value of log (q_e-q_t) plotted against t (min), qe and K_1 was computed from the slope and intercept of the graph and summarized in Table 4.10 . The result revealed that, although the adsorption of Cd (II) was fitted to the first order kinetic model with R^2 =0.9796, but theoretical qe (mg/g) =9.78 was not in good agreement with the obtained from the experiments (34.5 mg/g). So the first order model is not followed. This was also reported by Taty-Costodes *et al.* [92] who investigated the kinetic models for the removal of cadmium onto sawdust.

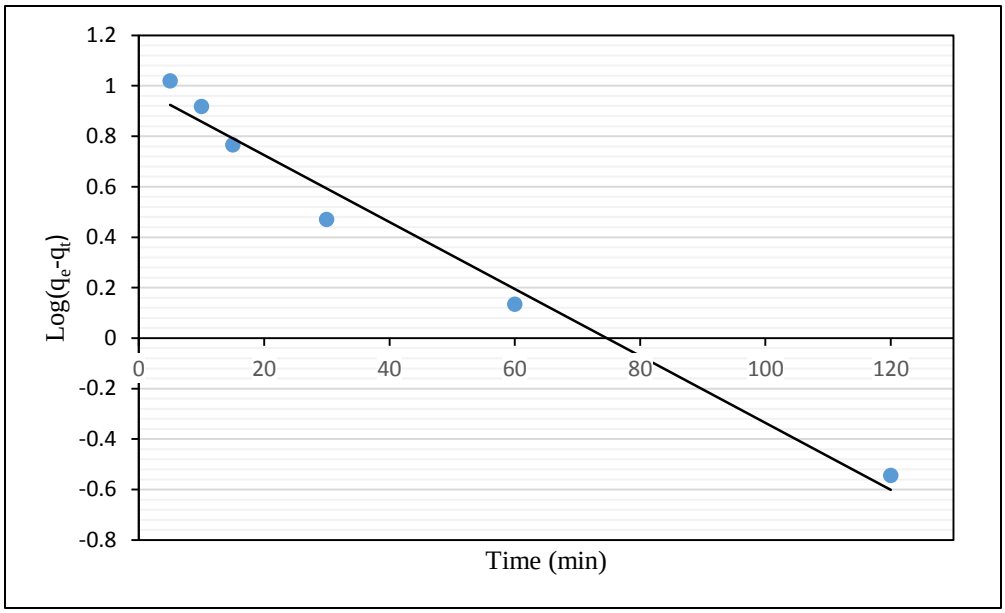


Figure 4.36: Pseudo-first-order kinetic Model for adsorption of cadmium from single solution

Table 4.10:Parameters of psudo-first-order for for adsorption of cadmium from single solution

R^2	K_1 (1/min)	q_e (mg/g) Theoretical	q_e (mg/g)Experimental
0.9796	0.03054263	9.783943931	34.5

The pseudo-second-order kinetic model was also fitted to the adsorption data of cadmium in single solution using the following formula

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} * t \qquad (4.4)$$

Where q_e is equilibrium adsorption capacity (mg/g), q_t (mg/g) adsorption capacity at time t (min), and K_2 (g/mg min) is pseudo-second-order constant rate. From the plot of t against t/q as shown in Figure 4.37, the parameters of this model K_2 and qe were computed from the slope and intercept of the graph. Table 4.11summarizes the model parameters. The results indicated perfect fitting and better than first order model where R^2 was found to be 0.999. The theoretical q_e of this model is in perfect agreement with the experimental q_e values as shown in the table. Accordingly, it was concluded that the system of adsorption is pseudo second order kinetic model, which suggests chemical adsorption including electrons exchange between AC and cadmium ions. Similar findings were reported by Mohan et.al [104] and Bohli *et al.* [87] who studied the kinetic models for cadmium removal by AC derived from wood and olive stone respectively .

Table 4.11:Parameters of pseudo-second-order for adsorption of cadmium from single solution

R^2	K_2 (g/mg. min)	q_e (mg/g) Theoretical	q_e(mg/g)Experimental
0.999	0.00598	35.9	34.5

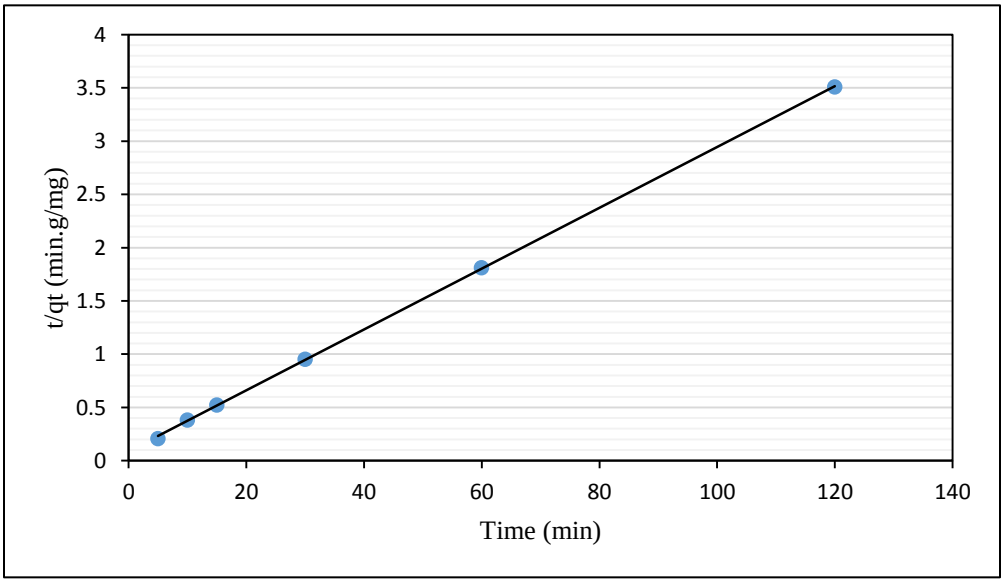


Figure 4.37:Second -order kinetic Model for adsorption of cadmium from single solution

4.2.3.2 Adsorption Kinetic Model for Lead in single metal adsorption

The experimental data of lead adsorption in single solution was also fitted to the pseudo-first-order and pseudo-second-order model using equations (4.3 & (4.4) as shown in Figure 4.38 & Figure 4.39 respectively. The parameters of both models were presented in table 4.12. The results revealed that, similar to cadmium, the pseudo-second order model was better fitted with higher correlation coefficient R^2 =0.9977 than pseudo-first order (R^2=0.975). In addition, the theoretical q_e of the pseudo-second order model is in perfect agreement with the experimental q_e values as shown in the table 4.12. .Therefore, the adsorption of lead from single solution follows pseudo-second order model. This is in good agreement with Depci *et al.*[105] who studied the removal of lead from single and competitive solution by AC derived from Van apple pulp.

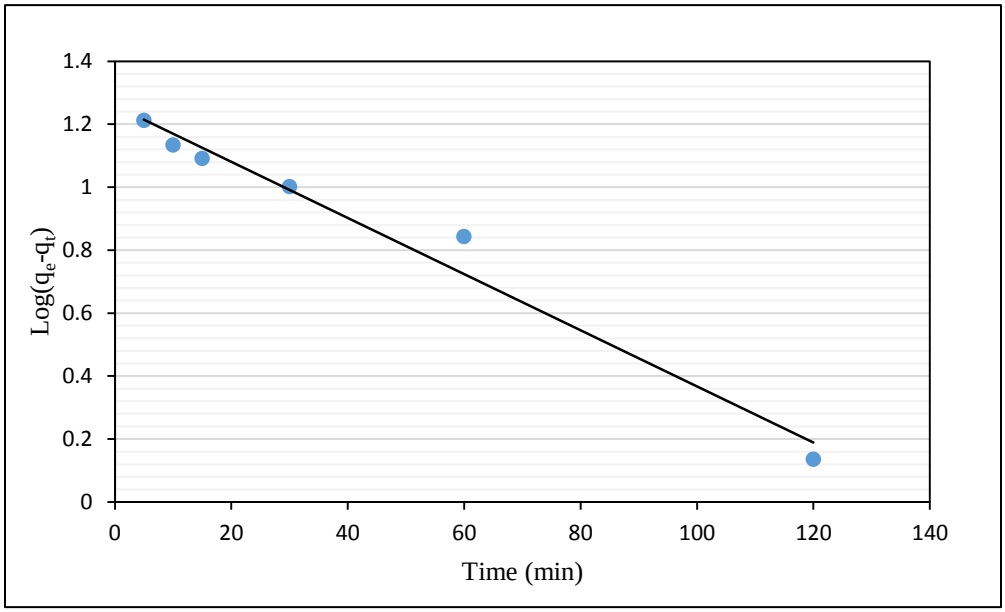


Figure 4.38 :Pseudo-first-order kinetic Model for adsorption of lead from single solution

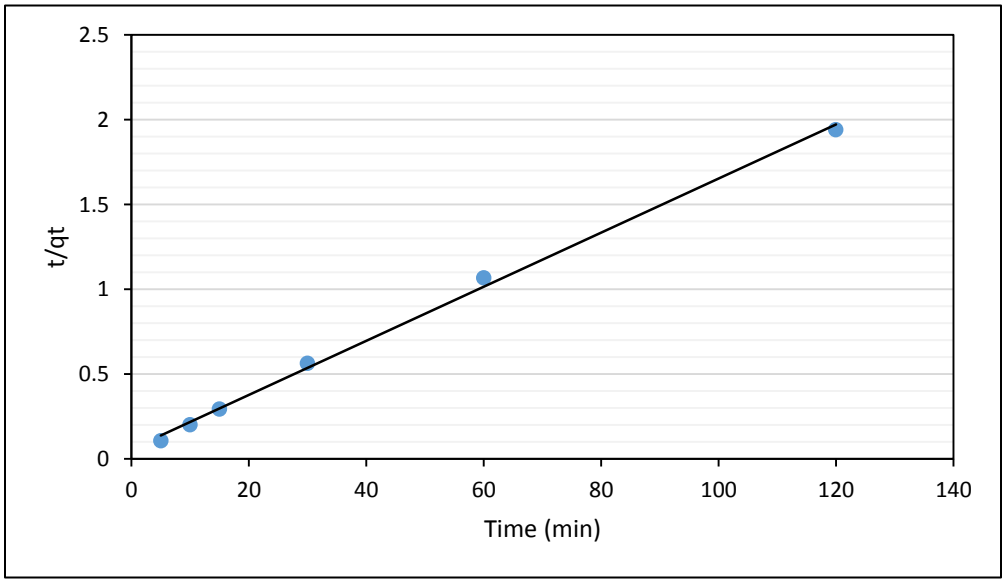


Figure 4.39:Pseudo-second-order kinetic Model for adsorption of lead from single solution

Table 4.12:Pseudo-first and second order parameters for lead adsorption from single solution

Kinetic Model	Pseudo-first-order	Pseudo-second-order
R^2	0.9751	0.9977
K	0.02054	0.0033
q_e (mg/g) Theoretical	18.184	64.36
q_e(mg/g)Experimental	63.2	63.2

4.3 Competitive adsorption of Cd (II) and Pb (II) on the Prepared AC

In this section the potentiality of the prepared activated carbon for the removal of heavy metals from synthetic industrial wastewater in binary aqueous medium of (Cd-Pb) will be investigated.

4.3.1.1 Effect of pH

The effect of pH on the removal efficiency of cadmium and lead from binary solutions was investigated where pH varied from 3-7 (3, 4, 5, 5.5, 6, and 7.0). Batch experiments were conducted at initial metal concentration of 100 mg/l for each metal in binary solution, 50 mg adsorbent dosage, 3.0 hours contact time, 50 ml solution volume and 200 rpm shaking speed. Removal efficiency of cadmium and lead ions at different pH values on prepared AC from binary synthetic solution are presented in Figure 4.40 .The obtained results showed that in both metals, when pH increased the removal efficiency also increased because at low pH values there is strong competition between hydrogen and metal ion, and this competition decrease with increase of pH. However at high pH values the precipitation of metal ions as hydroxide takes place as discussed before in single adsorption (see page 80). On the other hand, it was observed that significant drop in cadmium removal efficiency at same pH values comparing to removal efficiency in single solution, whereas insignificant change was observed in lead removal between single and competitive solutions. The removal efficiency of cadmium in single adsorption varied from 26% at pH=3.0 to 38% at pH=7, while in competitive adsorption varied from 10% at pH=3.0 to 18.5% at pH =7.0. On the other hand, the removal of lead increased from 50 at pH=3 to 85% at pH= 7.0 in single solution whereas increased from

46 % at pH =3.0 to 84 % at pH=7.0 in competitive adsorption. This clearly shows that strong competition occurs between cadmium and lead ion for adsorbent sites at different pH values.

Removal efficiency of lead was much higher than cadmium in competitive adsorption at different pH values. This might be related to the ability of competition between these two metals. AC possess definite number of adsorption sites and these metals compete together , Pb (II) attached more strongly to AC than Cd (II) because of properties of each metal. Table 4.13 shows some important properties of each metal. In addition to the higher electronegativity and ionic radius of lead, it has lower hydrated radius, consequently it is easier to get to different microspores than cadmium. Qin *et al.*[106] studied the competitive adsorption of cadmium, lead and copper on peat. They reported that lead has the highest removal whereas cadmium has the lowest. They attributed this to the difference in electronegativity, ionic radius and hydrated ionic radius.

To avoid any precipitation at high pH values further experiments were carried out at pH values of 5.0. Optimum pH of 5.0 also observed by Bohli *et al.* [87] who studied the removal of cadmium, lead and copper from single and binary solution on AC from olive stone.

Table 4.13: properties of invetigated metals

Property	Lead	Cadmium	Ref.
Electronegativity (Pauling)	2.33	1.69	[87]
Hydrated ionic radius (Å)	4.01	4.26	[87]
Ionic radius (Å)	1.19	0.95	[87]

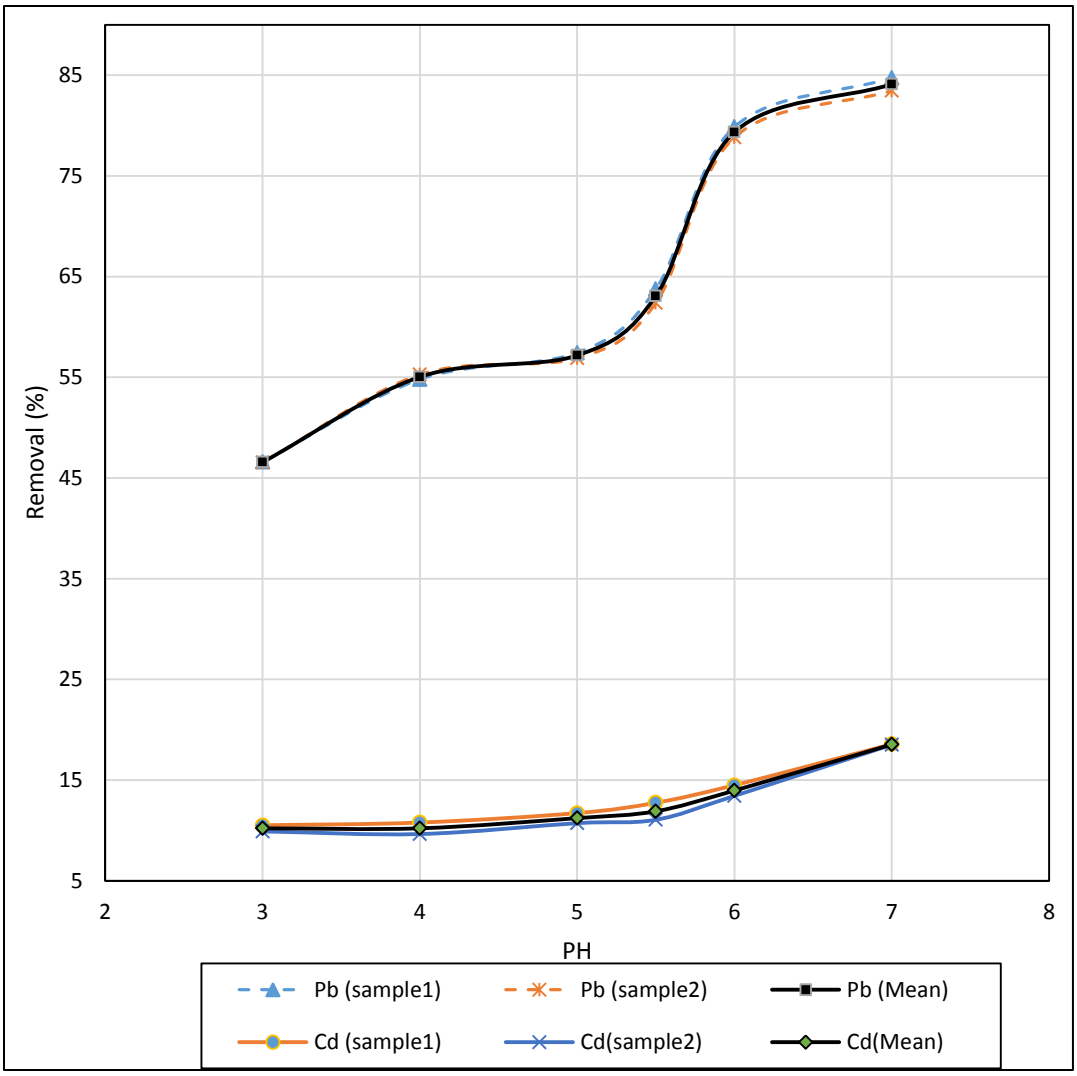


Figure 4.40:Effect of pH on Cd (II) and Pb (II) Removal Efficiency from competitive solution

4.3.1.2 Effect of Contact time

To investigate the effect of contact time on the removal efficiency of Cd (II) and Pb (II) in competitive mode by prepared AC, batch experiments were performed at different times in range 5.0-1920 minutes under the following constant conditions; pH =5.0, initial metal concentration of 100 mg/l for each, adsorbent dosage 50 mg /50 ml of solution.

The same trend of single equilibrium time was observed in the competitive adsorption of Cd (II) and Pb (II) as shown in Figure 4.41. After 120 minutes almost constant removal observed indicating that equilibrium time is reached as discussed before (see page 85). However lower removal efficiency was observed, where the maximum removal obtained at the equilibrium was around 22.5 % and 54 % for Cd (II) and Pb (II) respectively while it was around 34% and 61% in single solution. This may be related to the competition between Pb (II) and Cd (II) as explained before (see page 109 . Further adsorption experiments were carried out using 180 minutes as contact time to emphasize that equilibrium is reached.

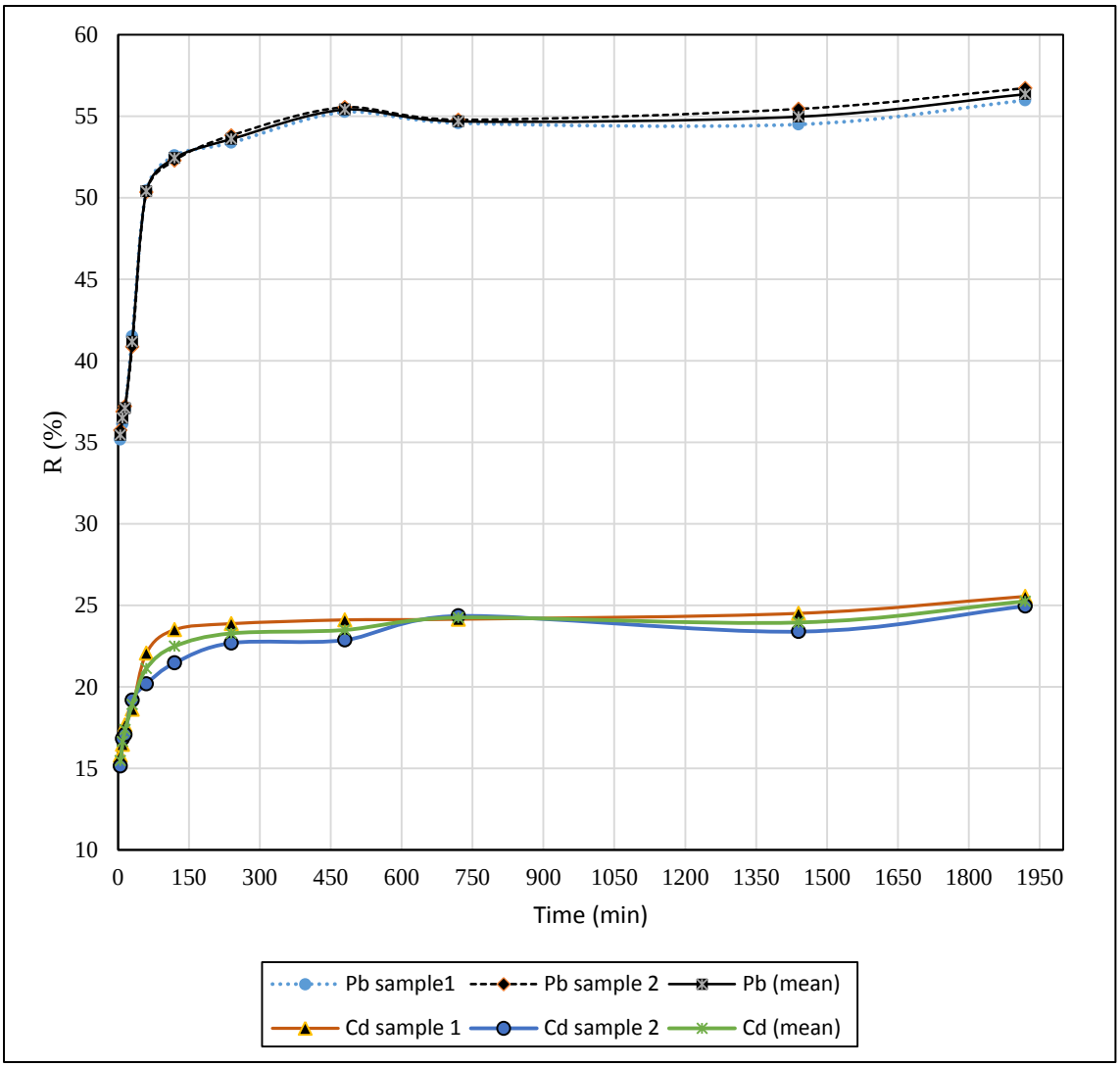


Figure 4.41:Effect of contact time on Cd(II)- Pb (II) efficiency removal in competitive mode

4.3.1.3 Effect of Initial concentration

To investigate the effect of initial concentration on the removal efficiency of Cd (II) and Pb (II) in competitive mode by prepared AC, batch experiments were performed at different initial concentrations in range of (25- 300) mg/l as shown in

Table 3.4 ; contact time 180 minutes; pH =5.0, and adsorbent dosage 50 mg /50 ml of solution. The effect of initial concentration on the removal efficiency and adsorption capacity of cadmium and lead on prepared AC are presented in figures (4.40-4.43).

Figure 4.42 & Figure 4.43 shows the effect of initial concentration of cadmium in presence of different concentration of lead on the removal efficiency and adsorption capacity of cadmium respectively. Whereas Figure 4.44 & Figure 4.45 shows the effect of initial concentration of lead at presence of different concentration of cadmium on the removal efficiency and adsorption capacity of lead respectively. For both metals the increase in the initial concentration led to increase the adsorption capacity and decrease the removal efficiency. This is in line with the effect of initial concentration of single adsorption as discussed before (see page 88). However, it was observed that adsorption capacity of cadmium in competitive mode decreased sharply in presence of lead as shown in Figure 4.43. The adsorption capacity of cadmium in single mode at initial concentration of 300 ppm was 56 mg/g. while, the adsorption capacity in competitive mode at the same initial concentration dramatically decreased to 28 mg/g, when Pb (II) increased from 0 to 25 ppm. When Pb (II) increased from 25 to 50 ppm, small decrease of Cd (II) adsorption capacity was noticed, while the behavior of adsorption capacity of

Pb (II) in competitive mode (Figure 4.45) also decreased due to the presence of Cd (II), but with steady fall. This might be related to the ability of competition between these two metals. AC possess definite number of adsorption sites and these metals compete together and Pb (II) attached more strongly to AC than Cd (II). This is because Pb (II) has higher electronegativity, higher ionic radius, and lower hydrated ionic radius than Cd as discussed before (see page 109). Consequently, AC sites has stronger physical and chemical affinity for lead than cadmium, which in consistence with single adsorption results. This was also reported by Qin *et al.* [106] who studied the removal of cadmium and lead from single and binary solutions. Moreover, the interaction forces between carbon and cadmium are weaker and cadmium ions are attached to only surface centers that have high negative charge density as reported by Mohan *et al*. [107] who studied the removal of cadmium and copper from single and binary system. Similar results was obtained by Li *et al.* [108] who investigated the competitive adsorption of cadmium and lead by pretreated biomass .

According to Mohan and Singh [109] who studied multi component adsorption of heavy by activated carbon from bagasse, the adsorption behavior of competitive systems decrease, increase, or no change , which depends on the ratio between Q competitive and Q single, according to the following cases ; Q competitive / Q single > 1: increase, Q competitive / Q single <1: decrease, or Q competitive / Q single =1: no change . By applying this formula to the obtained results for both metals, it was found that Q competitive / Q single <1, so since the ratio between adsorption capacity in single solution and competitive solution at different concentration was less than 1.0, this

indicates that the adsorption capacity of cadmium and lead suppressed by presence of other metal.

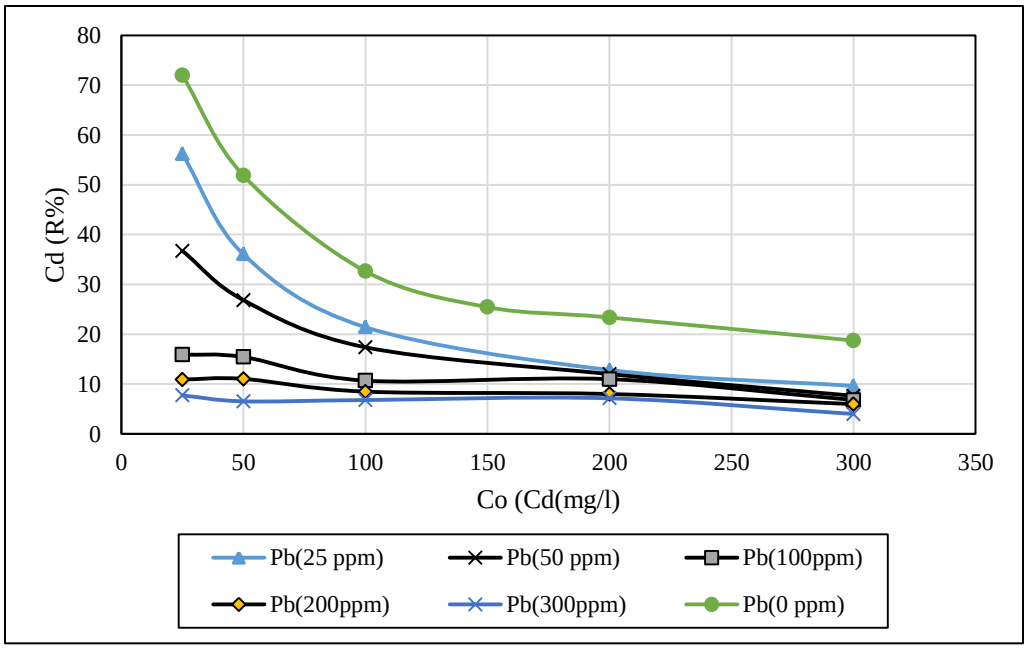


Figure 4.42:Effect of initial concentration on Cd (II) efficiency removal by AC in competitive mode

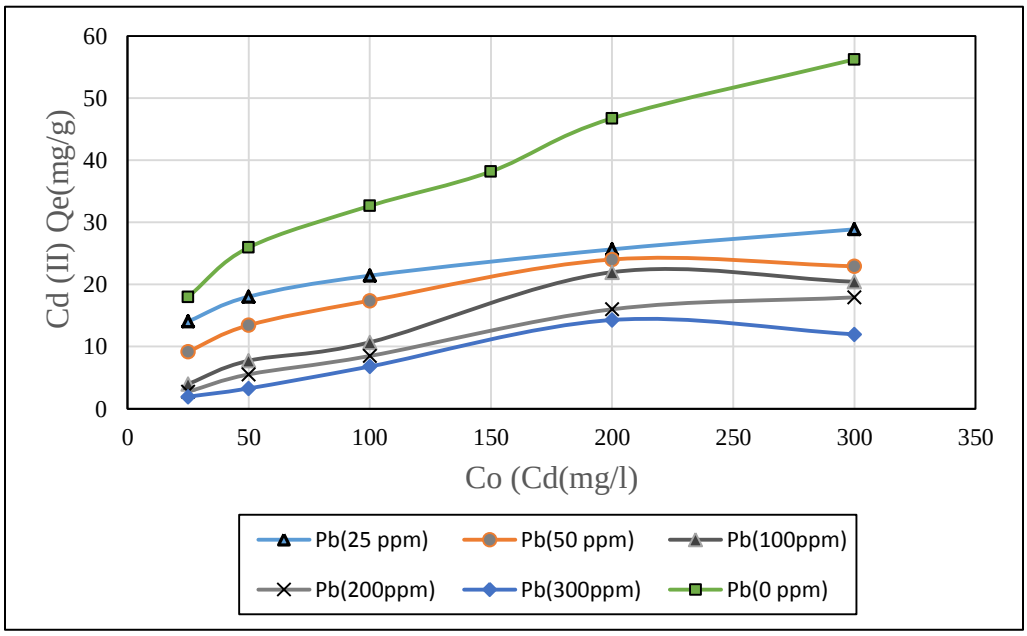


Figure 4.43:Effect of initial concentration on adsorption capacity of Cd (II) by AC in competitive mode

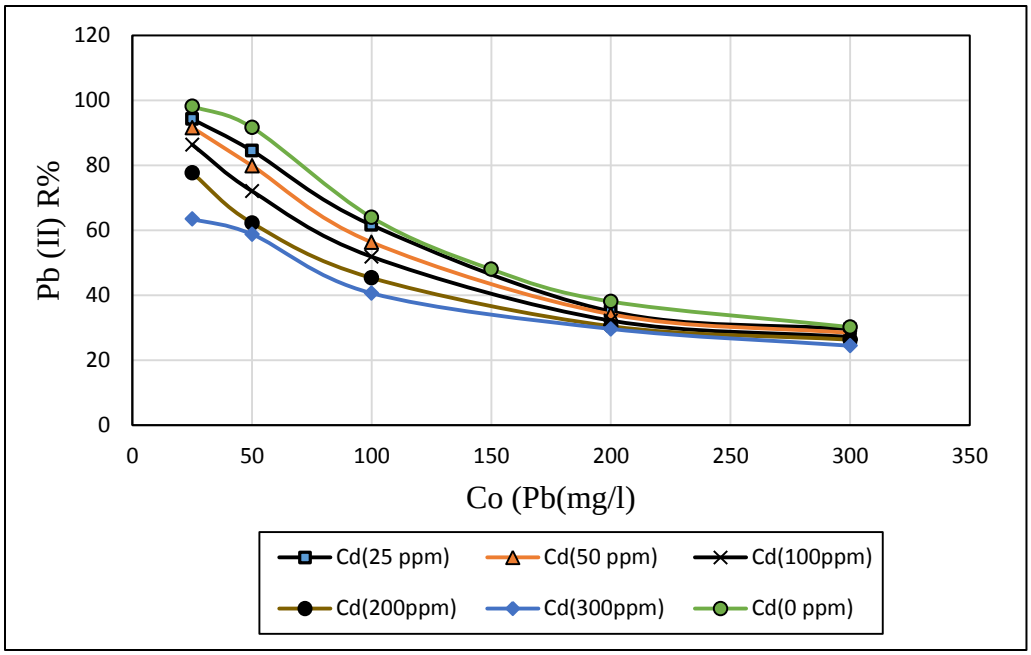


Figure 4.44:Effect of initial concentration on Pb (II) efficiency removal by AC in competitive mode

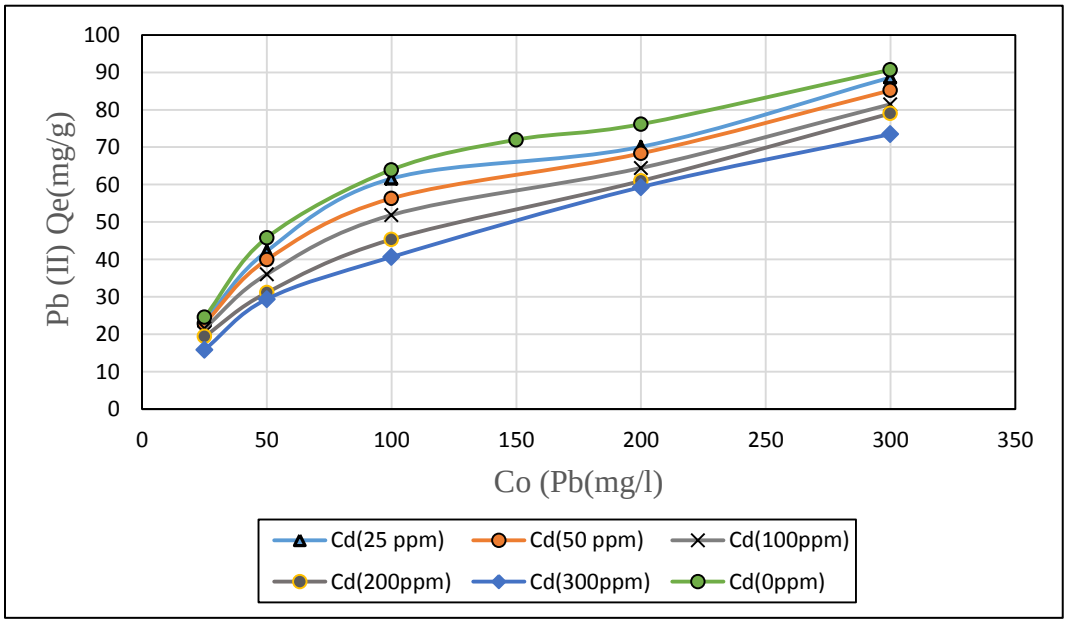


Figure 4.45:Effect of initial concentration on adsorption capacity of Pb (II) by AC in competitive mode

4.3.1.4 Effect of Adsorbent dosage

To investigate the effect of AC dosage on the removal efficiency of Cd (II) and Pb (II) in competitive mode by prepared AC, batch experiments were performed with different AC dosage from 25 to 400 mg (25, 50, 100, 200, 300 and 400), mg /50 ml at initial concentrations of 100 mg/l of each metal, contact time 180 minutes; pH =5.0

The effect of AC dosage on the removal efficiency and adsorption capacity of cadmium and lead in competitive solutions are illustrated in Figure 4.46 & Figure 4.47.When comparing the effect of AC dosage in single to competitive, almost the same trend of single mode was observed for lead removal and adsorption capacity. However, there was decrease in the removal efficiency as well as adsorption capacity of cadmium. At AC dosage of 300 mg the removal efficiency dropped from 85 % to 70 % in single and competitive mode respectively. In addition, the adsorption capacity dropped from 43 mg/g to 10 mg/g in single and competitive mode respectively, which indicated that strong competition between cadmium and lead for AC sites takes place. Lead possess higher electronegativity and ionic radius and lower hydrated ionic radius as explained before (see page 109), as a result, large number of AC adsorption sites were occupied by lead ions.

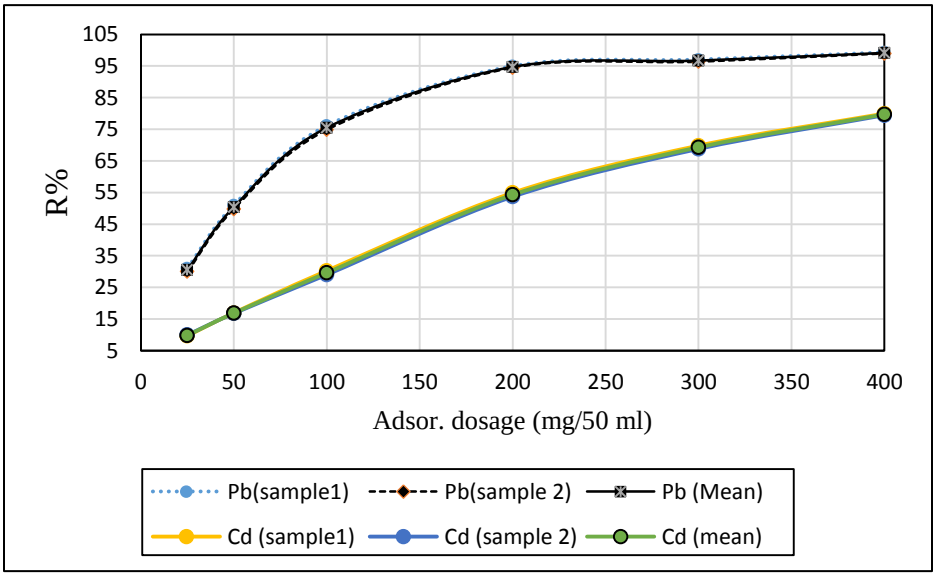


Figure 4.46:Effect of AC dosage on removal efficiency of Cd (II) and Pb (II) in competetive mode

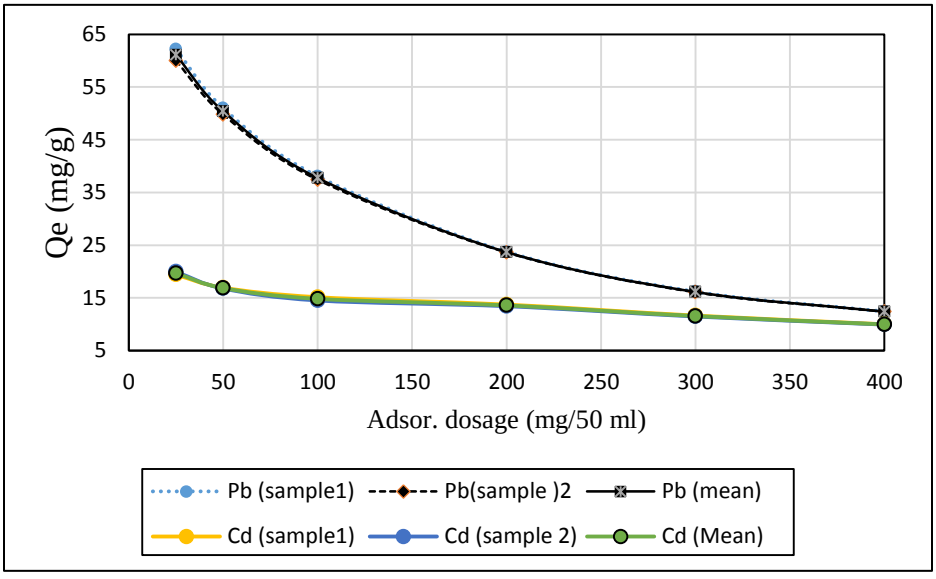


Figure 4.47:Effect of AC dosage on Adsorption capacity of Cd (II) and Pb (II) in competitive mode

4.3.1 Adsorption Equilibrium Isotherms

The obtained experimental data for cadmium and lead adsorption in competitive system on prepared AC from household organic waste was fitted to isotherm models of Langmuir and Freundlich.

4.3.1.1 Adsorption Equilibrium Isotherms for Cadmium in competitive metal adsorption

The experimental data of cadmium adsorption in presence of different concentration of lead was fitted to Langmuir and Freundlich isotherms as shown in Figure 4.48 & Figure 4.49, and the parameters of each model were calculated and presented in Tables (4.14) and (4.15) respectively. The correlation coefficients of both isotherms indicated that good fitting was observed in general, but Freundlich isotherm was fitted better with increasing the concentration of lead. The results also showed that the affinity factor for Langmuir isotherms ($a_{l)}$ decreases with increasing the concentration of lead indicating that strong competition between metal ions takes place for adsorption sites. This is in consistence with the decrease in adsorption intensity factor of Freundlich isotherm (K_f) as the concentration of lead increase. Similar findings were reported by Mohan and Singh [109] and Mohan *et al.* [107] who studied the adsorption of cadmium from competitive solution onto Kraft lignin and AC from bagasse respectively.

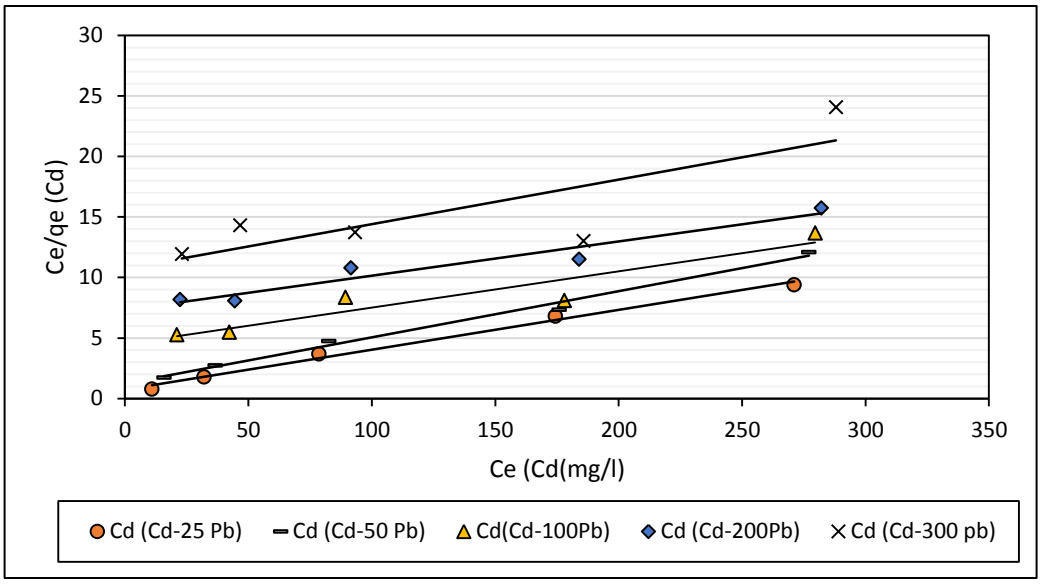


Figure 4.48:Langmuir isotherm of AC for cadmium adsorption from competitive solution

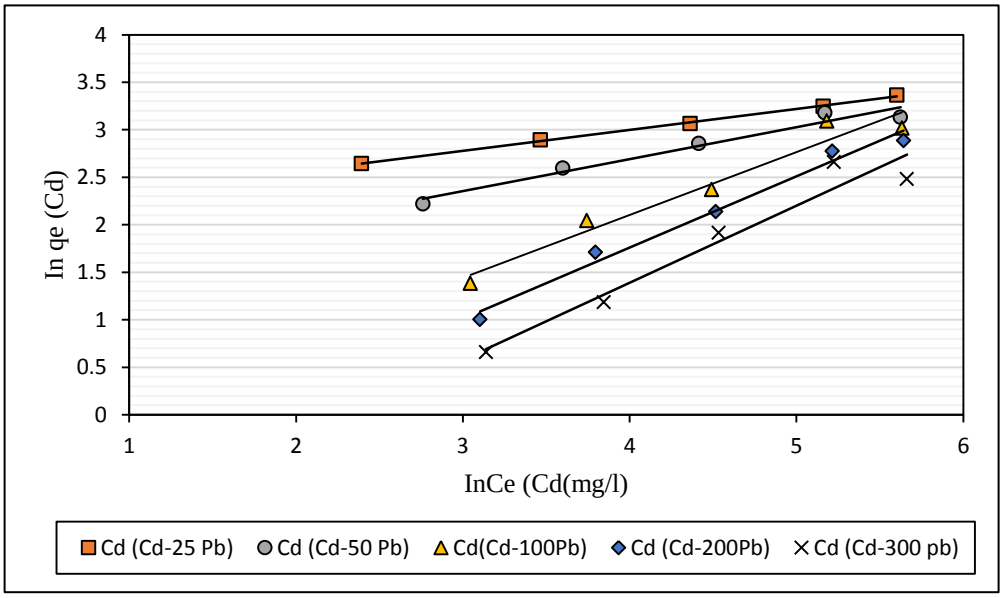


Figure 4.49:Freundlich isotherm of AC for cadmium adsorption from competitive solution

Table 4.14:Isotherm Parameters of Langmuir for Cd (II) adsorption from competitive solution

Langmuir isotherm parameter (Cd)					
Cd(II)	Pb(II)				
	25	50	100	200	300
R^2	0.992	0.991	0.888	0.941	0.67
K_L(L/g)	1.3281	0.80988	0.22098	0.1366	0.09331
a_l	0.04367	0.0309	0.00662	0.00386	0.00344
Q_o	30.4094	26.2068	33.3887	35.3902	27.1556
R_L	0.1235	0.16606	0.48181	0.61455	0.6417

Table 4.15:Isotherm Parameters of Freundlich for Cd (II) adsorption from competitive solution

Freundlich isotherm parameter (Cd)					
Cd(II)	Pb(II)				
	25	50	100	200	300
R^2	0.998	0.96	0.9539	0.9839	0.9455
n	4.53907	2.96673	1.51184	1.33431	1.23252
K_f	8.30181	3.82749	0.58096	0.29038	0.15634

4.3.1.2 Adsorption Equilibrium Isotherms for Lead in competitive metal adsorption

The experimental data of lead adsorption in presence of different concentration of cadmium was also fitted to Langmuir and Freundlich isotherms as shown in Figure 4.50 &Figure 4.51, and the parameters of each model were calculated and presented in Tables (4.16) and (4.17) respectively. Similar to cadmium adsorption, the correlation coefficients of both isotherms indicated that good fitting was observed in general, but Freundlich isotherm was fitted better with increasing the concentration of cadmium. The results also showed that the affinity factor for Langmuir isotherms (a_l) decreases with increasing the concentration of cadmium indicating that strong competition between metal ions takes place for adsorption sites. This is in consistence with the decrease in adsorption intensity factor of Freundlich isotherm (K_f) as the concentration of cadmium increase. Similar findings were reported by Li *et al* [108], and Depci *et al.*[105] who investigated the adsorption of lead from competitive solution onto Phanerochaete chrysosporium and AC from van apple pulp respectively.

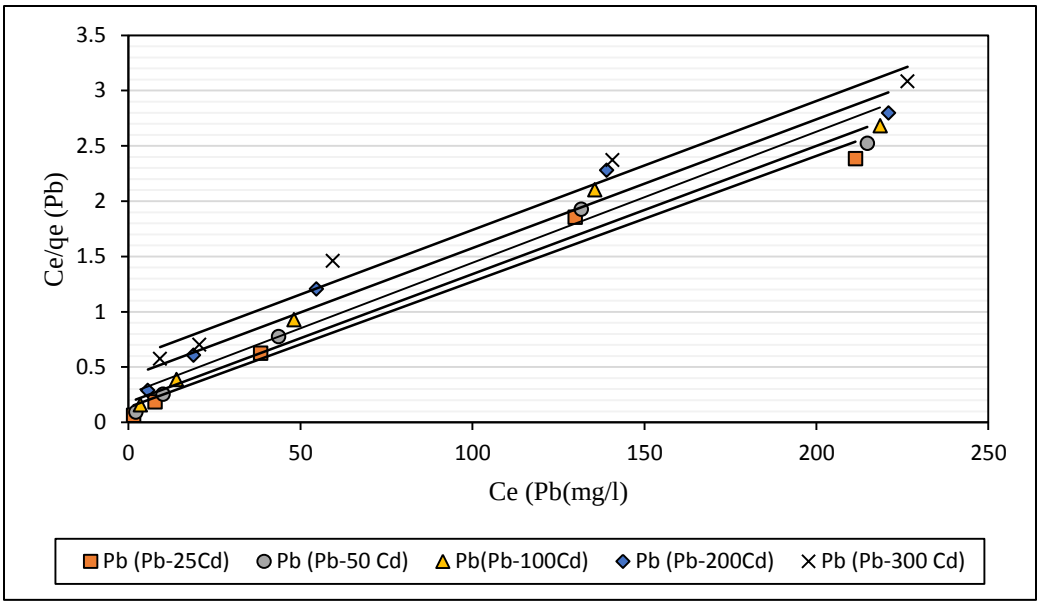


Figure 4.50:Langmuir isotherm of AC for lead adsorption from competitive solution

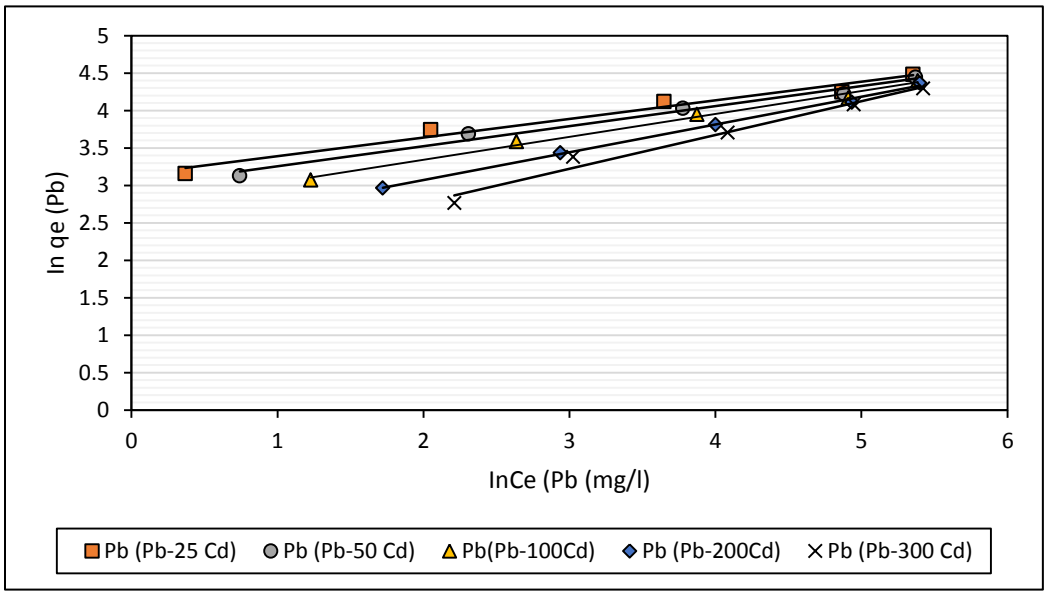


Figure 4.51:Frendlich isotherm of AC for lead adsorption from competitive solution

Table 4.16:Isotherm Parameters of Langmuir for Pb (II) adsorption from competitive solution

Langmuir isotherm parameter (Pb)					
Pb(II)	Cd(II)				
	25	50	100	200	300
R^2	0.978	0.9795	0.976	0.966	0.9777
K_L(L/g)	7.25761	5.53492	3.899	2.41999	1.7444
a_l	0.08244	0.06416	0.04625	0.02816	0.02035
Q_o	88.0332	86.2627	84.3095	85.9397	85.7081
R_L	0.06946	0.08752	0.11744	0.17934	0.23216

Table 4.17:Isotherm Parameters of Freundlich for Pb (II) adsorption from competitive solution

Freundlich isotherm parameter (Pb)					
Pb(II)	Cd(II)				
	25	50	100	200	300
R^2	0.9723	0.9849	0.9914	0.9966	0.977
n	4.0292	3.73042	3.27343	2.70143	2.21901
K_f	23.1749	19.8503	15.3708	10.3148	6.4977

4.3.2 Adsorption Kinetic Models

4.3.2.1 Adsorption Kinetic Models for Cadmium in Competitive metal adsorption

Pseudo-first-order and pseudo-second-order model was fitted to the experimental data of cadmium adsorption in competitive solution using equations (16 &17) as shown in Figure 4.52 & Figure 4.53 respectively. The parameters of both models were presented in Table 4.18. The results indicated that, similar to the behavior of cadmium in single solution, although the adsorption of Cd (II) was fitted to the first order kinetic model with R^2 =0.9932, but theoretical qe (mg/g) =8.02 was not in good agreement with the experimental adsorption capacity (23.2 mg/g). On the other hand, the pseudo-second order model was better fitted with higher correlation coefficient R^2 =0.9977 and the theoretical qe of this model (23.74 mg/g) is in perfect agreement with the experimental qe value as shown in the Table 4.18. Therefore, the adsorption of cadmium from competitive solution follows pseudo-second order model. Similar findings were reported by Taty-Costodes *et al*.[92] and Mohan *et al.* [107] who investigated the removal of cadmium from competitive solutions onto Kraft lignin.

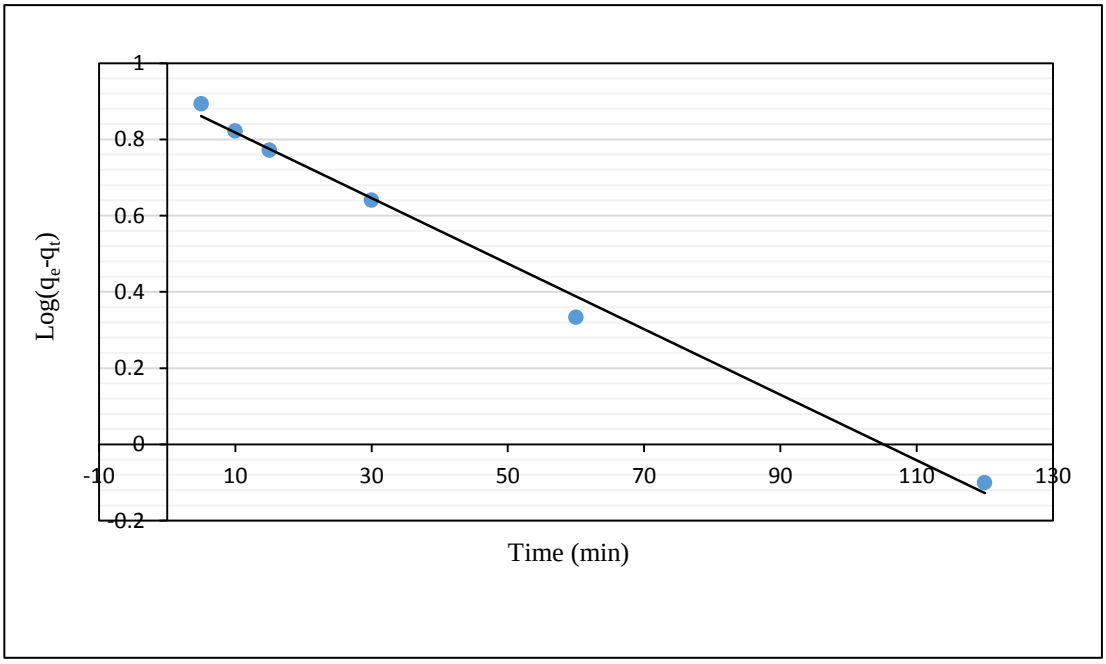


Figure 4.52:Pseudo-first-order kinetic Model for adsorption of cadmium from competetive solution

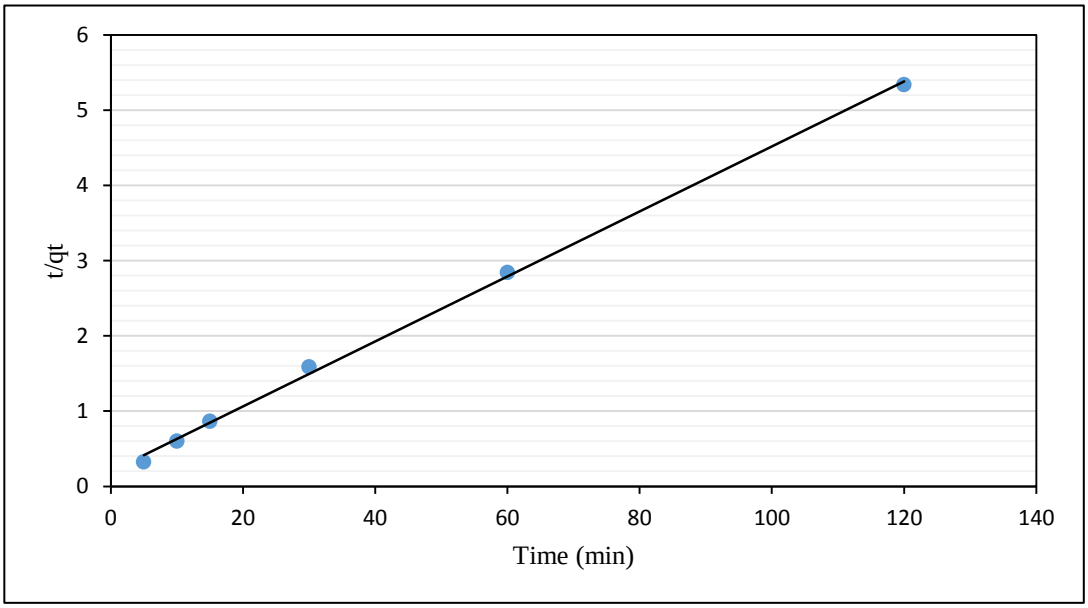


Figure 4.53:Pseudo-second-order kinetic Model for adsorption of cadmium from competitive solution

Table 4.18 :Pseudo-first and second order parameters for cadimum adsorption from competitive solution

Kinetic Model	Pseudo-first-order	Pseudo-second-order
R^2	0.9932	0.9987
K	0.0198	0.00758
q_e (mg/g) Theoretical	8.02	23.74
q_e(mg/g)Experimental	23.2	23.2

4.3.2.2 Adsorption Kinetic Models for Lead in Competitive metal adsorption

The experimental data of lead adsorption in competitive solution was also fitted to the pseudo-first-order and pseudo-second-order model using equations (16 &17) as shown in Figure 4.54 & Figure 4.55& respectively. The parameters of both models were presented in Table 4.19. The results revealed that, similar to cadmium, the pseudo-second order model was better fitted with higher correlation coefficient R^2 =0.997 than pseudo-first order (R^2=0.966). In addition, the theoretical adsorption capacity of this model is in perfect agreement with the experimental one as shown in the Table 4.19. Therefore, the adsorption of lead from competitive solution follows pseudo-second order model. Similar findings were reported by Bohli *et al.* [87] and Depci *et al*. [105], who investigated the adsorption of lead from competitive solution by AC prepared from olive stone and van apple pulp respectively.

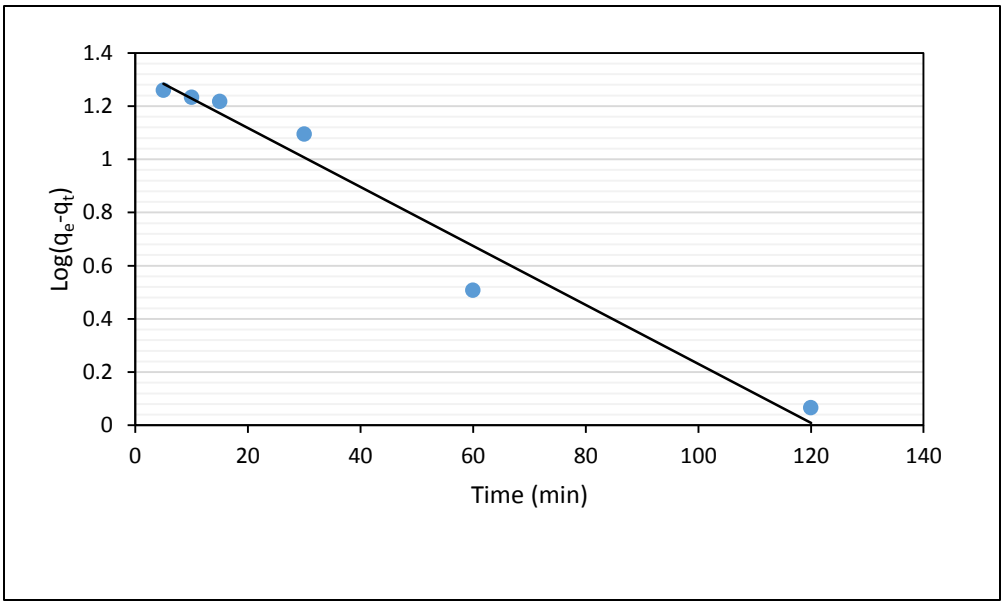


Figure 4.54:Pseudo-first-order kinetic Model for adsorption of lead from competetive solution

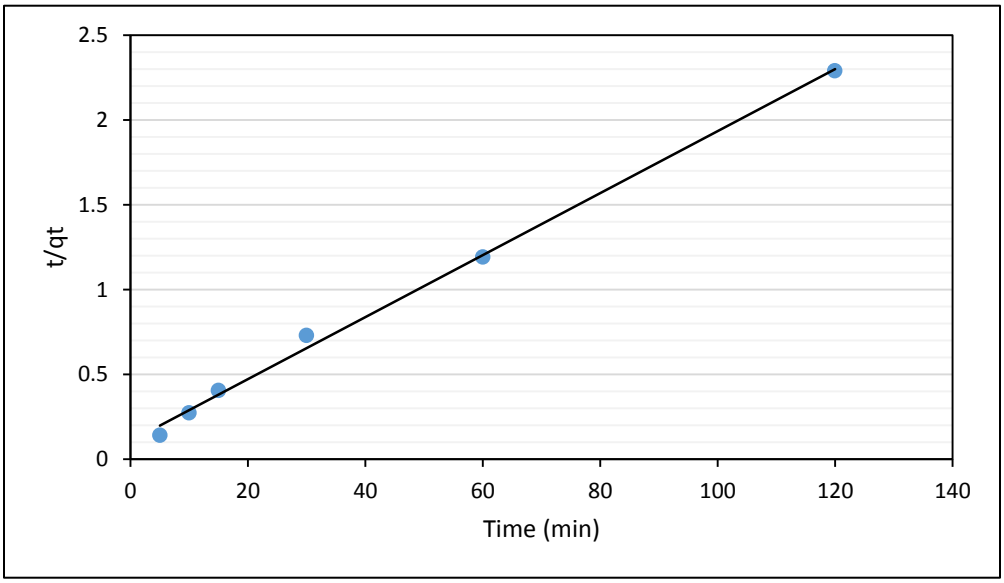


Figure 4.55:Pseudo-second-order kinetic Model for adsorption of lead from competitive solution

Table 4.19:Pseudo-first and second order parameters for lead adsorption from competitive solution

Kinetic Model	Pseudo-first-order	Pseudo-second-order
R^2	0.9662	0.997
K	0.0255	0.0025
q_e (mg/g) Theoretical	21.868	55.98
q_e(mg/g)Experimental	53.6	53.6

CONCLUSION

In conclusion, household organic waste is abundant and rich in carbon, so, in this study, it was utilized as potential low cost source of activated carbon, Activated carbon was prepared through chemical activation process using two activating agents, namely potassium hydroxide and phosphoric acid. The activation process with phosphoric acid showed better characteristics of prepared AC in terms of yield and porosity. The precursor was carbonized at different temperatures, times, and impregnation ratios. The produced activated carbon was characterized by the standard methods. At the best activation conditions, temperature of 700 C, time of 2 hours, and impregnation ratio of 30 %.,highest surface area obtained was around 790 m^2/g. The produced AC was tested for its performance in heavy metals removal from synthetic industrial wastewater through adsorption experiments. The adsorption experiments were conducted in the batch mode and concentrated on the adsorption of Cadmium (Cd) and Lead (Pb) ions from synthetic solutions in single as well as binary systems. The effect of operational parameters such as contact time, pH, and adsorbent dosage on the adsorption behavior was also investigated. The experimental data of adsorption was fitted to Langmuir and Freundlich, where good fitting was observed. The isotherms also showed that the maximum adsorption capacity of cadmium was found to be 61 mg/g and 90 mg/g for lead at equilibrium time of 120 minutes. The experimental data of adsorption was also fitted to pseudo-first-order and pseudo -second-order kinetic models. Furthermore, in all experiments, it was observed the adsorption capacity and removal efficiency of lead is better than cadmium. The

adsorption capacities on prepared AC was ordered as Pb (II)>Pb (II) (Cd-Pb)>Cd (II)>Cd (II) (Cd-Pb).

FUTURE WORK

At the end of this experimented work some extra work should be conducted:

- Exploring the preparation of activated carbon from household organic waste using physical method.
- Investigate different activating agents, for example, zinc chloride and sulfuric acid.
- Investigate different impregnation rather than that used in this study.
- Investigate the preparation of activated carbon under flow of nitrogen.
- Investigate the adsorption of other metals on the prepared carbon.
- Investigate different parameters of adsorption.

References

[1] L. S. Thakur and M. Parmar, “Adsorption of Heavy Metal (Cu2+, Ni2+ and Zn2+) from Synthetic Waste Water by Tea Waste Adsorbent,” vol. 2, no. 6, pp. 6–19, 2013.

[2] M. M. Rahman, M. Adil, A. M. Yusof, Y. B. Kamaruzzaman, and R. H. Ansary, “Removal of heavy metal ions with acid activated carbons derived from oil palm and coconut shells,” *Materials (Basel).*, vol. 7, no. 5, pp. 3634–3650, 2014.

[3] T. a H. Nguyen, H. H. Ngo, W. S. Guo, J. Zhang, S. Liang, Q. Y. Yue, Q. Li, and T. V Nguyen, “Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater.,” *Bioresour. Technol.*, vol. 148, pp. 574–85, Nov. 2013.

[4] M. a. Barakat, “New trends in removing heavy metals from industrial wastewater,” *Arab. J. Chem.*, vol. 4, no. 4, pp. 361–377, 2011.

[5] D. Mohan, A. Sarswat, Y. S. Ok, and C. U. Pittman, “Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - A critical review.,” *Bioresour. Technol.*, pp. 1–12, Feb. 2014.

[6] H. Reynel-Avila, “Multicomponent removal of heavy metals from aqueous solution using low-cost sorbents,” *Water Prod. …*, 2011.

[7] M. A. Habila, Z. A. ALOthman, R. Ali, A. A. Ghafar, and M. S. E.-D. Hassouna, “Removal of Tartrazine Dye onto Mixed-Waste Activated Carbon: Kinetic and Thermodynamic Studies,” *CLEAN - Soil, Air, Water*, vol. 42, no. 9999, p. n/a–n/a, Apr. 2014.

[8] H. U. Khan, T. Husain, and S. M. Khan, “Solid Waste Management Practices in the Eastern Province of Saudi Arabia,” *Environ. Manage.*, vol. 11, no. 6, pp. 729–734, Nov. 1987.

[9] G. Gardner, “Recycling organic wastes.,” pp. 1–10, 1998.

[10] A. Bhatnagar and M. Sillanpää, “Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—A review,” *Chem. Eng. J.*, vol. 157, no. 2–3, pp. 277–296, Mar. 2010.

[11] C. Sawyer, P. Mccarty, and G. Parkin, *Chemistry for Environmental Engineering and Science .pdf*, Fifth edit. New Yourk: McGraw-Hill Education, 2003.

[12] S. Faust and O. Aly, “Adsorption processes for water treatment,” 1987.

[13] a Dabrowski, “Adsorption--from theory to practice.,” *Adv. Colloid Interface Sci.*, vol. 93, no. 1–3, pp. 135–224, Oct. 2001.

[14] M. Letnam, *Adsorption.pdf*, Second edi. New Yourk: McGraw-Hill Education, 1951.

[15] K. Y. Foo and B. H. Hameed, “Insights into the modeling of adsorption isotherm systems,” *Chem. Eng. J.*, vol. 156, no. 1, pp. 2–10, Jan. 2010.

[16] F. Çeçen and Ö. Aktas, *Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment*. 2011.

[17] R. Bansal and M. Goyal, *Activated carbon adsorption*. 2005.

[18] T. Hill, “Theory of physical adsorption,” *Adv. Catal*, vol. 4, pp. 211–258, 1952.

[19] J. M. Dias, M. C. M. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla, and M. Sánchez-Polo, “Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review.,” *J. Environ. Manage.*, vol. 85, no. 4, pp. 833–46, Dec. 2007.

[20] C. Moreno-Castilla and J. Rivera-Utrilla, “Carbon materials as adsorbents for the removal of pollutants from the aqueous phase,” *MRS Bull.*, no. November, pp. 890–894, 2001.

[21] K. Kadirvelu, K. Thamaraiselvi, and C. Namasivayam, “Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste.,” *Bioresour. Technol.*, vol. 76, no. 1, pp. 63–5, Jan. 2001.

[22] F.-C. Wu and R.-L. Tseng, “Preparation of highly porous carbon from fir wood by KOH etching and CO2 gasification for adsorption of dyes and phenols from water.,” *J. Colloid Interface Sci.*, vol. 294, no. 1, pp. 21–30, Feb. 2006.

[23] A. Baçaoui, A. Yaacoubi, and A. Dahbi, “Optimization of conditions for the preparation of activated carbons from olive-waste cakes,” *Carbon N. Y.*, vol. 39, pp. 425–432, 2001.

[24] M. H. de Oliveira Sampa, P. R. Rela, A. Las Casas, M. N. Mori, and C. L. Duarte, “Treatment of industrial effluents using electron beam accelerator and adsorption with activated carbon: a comparative study,” *Radiat. Phys. Chem.*, vol. 71, no. 1–2, pp. 459–462, Sep. 2004.

[25] H. Stoeckli, “Microporous carbons and their characterization: the present state of the art,” *Carbon N. Y.*, 1990.

[26] E. Leimkuehler, “Production, characterization, and applications of activated carbon,” no. May, 2010.

[27] S. Babel and T. A. Kurniawan, “Low-cost adsorbents for heavy metals uptake from contaminated water: a review.,” *J. Hazard. Mater.*, vol. 97, no. 1–3, pp. 219–43, Feb. 2003.

[28] H. Marsh, D. Yan, T. O’Grady, and a Wennerberg, “Formation of active carbons from cokes using potassium hydroxide,” *Carbon N. Y.*, vol. 22, no. 6, pp. 603–611, 1984.

[29] F. Edition, “Guidelines for Drinking-water Quality,” *World Health*, vol. 1, no. 3, pp. 104–8, 2011.

[30] L. Khezami and R. Capart, “Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies.,” *J. Hazard. Mater.*, vol. 123, no. 1–3, pp. 223–31, Aug. 2005.

[31] M. Ahmedna, W. E. Marshall, and R. M. Rao, “Production of granular activated carbons from select agricultural by-products and evaluation of their physical , chemical and adsorption properties,” *Bioresour. Technol.*, vol. 71, pp. 113–123, 2000.

[32] B. Dhir, “Potential of biological materials for removing heavy metals from wastewater.,” *Environ. Sci. Pollut. Res. Int.*, vol. 21, no. 3, pp. 1614–27, Feb. 2014.

[33] C. MAHAJAN, “REMOVAL OF HEAVY METALS FROM WINERY WASTEWATER BY USING NATURAL ADSORBENTS.,” *Int. …*, vol. 5, no. 1, pp. 69–78, 2014.

[34] F. Gönen and D. S. Serin, “Adsorption study on orange peel: Removal of Ni(II) ions from aqueous solution,” *African J. Biotechnol.*, vol. 11, no. 5, pp. 1250–1258, Jan. 2012.

[35] a B. Pérez-Marín, a Ballester, F. González, M. L. Blázquez, J. a Muñoz, J. Sáez, and V. M. Zapata, “Study of cadmium, zinc and lead biosorption by orange wastes using the subsequent addition method.,” *Bioresour. Technol.*, vol. 99, no. 17, pp. 8101–6, Nov. 2008.

[36] N. Feng, X. Guo, S. Liang, Y. Zhu, and J. Liu, “Biosorption of heavy metals from aqueous solutions by chemically modified orange peel.,” *J. Hazard. Mater.*, vol. 185, no. 1, pp. 49–54, Jan. 2011.

[37] N. Feng and X. Guo, “Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel,” *Trans. Nonferrous Met. Soc. China*, vol. 22, no. 5, pp. 1224–1231, May 2012.

[38] X. Li, Y. Tang, X. Cao, D. Lu, F. Luo, and W. Shao, “Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 317, no. 1–3, pp. 512–521, Mar. 2008.

[39] F. a Pavan, I. S. Lima, E. C. Lima, C. Airoldi, and Y. Gushikem, “Use of Ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions.,” *J. Hazard. Mater.*, vol. 137, no. 1, pp. 527–33, Sep. 2006.

[40] G. Annadural, R. S. Juang, and D. J. Lee, “Adsorption of heavy metals from water using banana and orange peels.,” *Water Sci. Technol.*, vol. 47, no. 1, pp. 185–90, Jan. 2003.

[41] M. Ashraf, A. Wajid, K. Mahmood, M. Maah, and I. Yusoff, “Low cost biosorbent banana peel (Musa sapientum) for the removal of heavy metals,” *Sci. Res. …*, vol. 6, no. 19, pp. 4055–4064, 2011.

[42] J. R. Memon, S. Q. Memon, M. I. Bhanger, G. Z. Memon, a El-Turki, and G. C. Allen, “Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal.,” *Colloids Surf. B. Biointerfaces*, vol. 66, no. 2, pp. 260–5, Oct. 2008.

[43] J. R. Memon, S. Q. Memon, M. I. Bhanger, A. El-Turki, K. R. Hallam, and G. C. Allen, “Banana peel: a green and economical sorbent for the selective removal of Cr(VI) from industrial wastewater.,” *Colloids Surf. B. Biointerfaces*, vol. 70, no. 2, pp. 232–7, May 2009.

[44] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, and S. Pattabhi, “Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions.,” *Bioresour. Technol.*, vol. 87, no. 1, pp. 129–32, Mar. 2003.

[45] E. El-Ashtoukhy, N. Amin, and O. Abdelwahab, “Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent,” *Desalination*, vol. 223, pp. 162–173, 2008.

[46] H. Arslanoglu, H. Soner Altundogan, and F. Tumen, “Preparation of cation exchanger from lemon and sorption of divalent heavy metals.,” *Bioresour. Technol.*, vol. 99, no. 7, pp. 2699–705, May 2008.

[47] M. Iqbal, A. Saeed, and S. I. Zafar, “FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding

the mechanism of Cd(2+) and Pb(2+) removal by mango peel waste.," *J. Hazard. Mater.*, vol. 164, no. 1, pp. 161–71, May 2009.

[48] K. Banerjee and S. Ramesh, "A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions," *J. Environ. Heal. Sci. ...*, vol. 3, no. 2, pp. 143–156, 2012.

[49] T. Aman, A. A. Kazi, M. U. Sabri, and Q. Bano, "Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent.," *Colloids Surf. B. Biointerfaces*, vol. 63, no. 1, pp. 116–21, May 2008.

[50] G. M. Taha, a. E. Arifien, and S. El-Nahas, "Removal Efficiency of Potato Peels As a New Biosorbent Material for Uptake of Pb(Ii) Cd(Ii) and Zn(Ii) From Their Aqueous Solutions," *J. Solid Waste Technol. Manag.*, vol. 37, no. 2, pp. 128–140, May 2011.

[51] S. O. Saka C. Demir H., Kahyaoglu M., "Removal of lead(II) from aqueous solutions using pre-boiled and formaldehyde-treated onion skins as a new adsorbent," *Sep. Sci. Technol. Sep. Sci. Technol.*, vol. 46, no. 3, pp. 507–517, 2011.

[52] P. Kumar and S. S. Dara, "Binding heavy metal ions with polymerized onion skin," *J. Polym. Sci. Polym. Chem. Ed.*, vol. 19, no. 2, pp. 397–402, Feb. 1981.

[53] D. C. K. Ko, C. W. Cheung, K. K. H. Choy, J. F. Porter, and G. McKay, "Sorption equilibria of metal ions on bone char.," *Chemosphere*, vol. 54, no. 3, pp. 273–81, Jan. 2004.

[54] C. W. Cheung, J. F. Porter, and G. Mckay, "Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char.," *Water Res.*, vol. 35, no. 3, pp. 605–12, Mar. 2001.

[55] C. W. Cheung, J. F. Porter, and G. McKay, "Sorption kinetics for the removal of copper and zinc from effluents using bone char," *Sep. Purif. Technol.*, vol. 19, no. 1–2, pp. 55–64, Jun. 2000.

[56] J. Yu, M. Tong, X. Sun, and B. Li, "Enhanced and selective adsorption of Pb2+ and Cu2+ by EDTAD-modified biomass of baker's yeast.," *Bioresour. Technol.*, vol. 99, no. 7, pp. 2588–93, May 2008.

[57] M. Song, M. Tang, S. Lv, X. Wang, B. Jin, Z. Zhong, and Y. Huang, "The pyrolysis of multi-component municipal solid waste in fixed bed reactor for activated carbon production," *J. Anal. Appl. Pyrolysis*, 2014.

[58] Y. Sudaryanto, S. B. Hartono, W. Irawaty, H. Hindarso, and S. Ismadji, “High surface area activated carbon prepared from cassava peel by chemical activation.,” *Bioresour. Technol.*, vol. 97, no. 5, pp. 734–9, Mar. 2006.

[59] M. Adib, Z. Al-qodah, and C. W. Z. Ngah, “Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production : A review,” *Renew. Sustain. Energy Rev.*, vol. 46, pp. 218–235, 2015.

[60] O. A. Ekpete and M. Horsfall, “Preparation and characterization of activated carbon derived from fluted pumpkin stem waste (Telfairia occidentalis Hook F),” *Res J Chem Sci*, vol. 1, no. 3, pp. 10–17, 2011.

[61] S. Brunauer, P. H. Emmett, and E. Teller, “Adsorption of Gases in Multimolecular Layers,” *J. Am. Chem. Soc.*, vol. 60, no. 2, pp. 309–319, 1938.

[62] R. H. Hesas, A. Arami-Niya, W. M. A. Wan Daud, and J. N. Sahu, “Preparation and characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: Application in methylene blue adsorption,” *BioResources*, vol. 8, no. 2, pp. 2950–2966, 2013.

[63] A.-N. a. El-Hendawy, A. J. Alexander, R. J. Andrews, and G. Forrest, “Effects of activation schemes on porous, surface and thermal properties of activated carbons prepared from cotton stalks,” *J. Anal. Appl. Pyrolysis*, vol. 82, no. 2, pp. 272–278, 2008.

[64] H. Sayğılı, F. Güzel, and Y. Önal, “Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption,” *J. Clean. Prod.*, vol. 93, pp. 84–93, 2015.

[65] P. Y. L. Foo and L. Y. Lee, “Preparation of Activated Carbon from Parkia Speciosa Pod by Chemical Activation,” vol. II, pp. 20–22, 2010.

[66] K. K. Alau, C. E. Gimba, and J. a Kagbu, “Preparation of Activated Carbon from Neem (Azadirachta indica) Husk by Chemical Activation with H 3 PO 4 , KOH and ZnCl 2,” vol. 2, no. 5, pp. 451–455, 2010.

[67] W. T. Tsai, C. Y. Chang, S. Y. Wang, C. F. Chang, S. F. Chien, and H. F. Sun, “Cleaner production of carbon adsorbents by utilizing agricultural waste corn cob,” *Resour. Conserv. Recycl.*, vol. 32, no. 1, pp. 43–53, 2001.

[68] J. Wang, F. Wu, M. Wang, N. Qiu, Y. Liang, and S. Fang, “Preparation of activated carbon from a renewable agricultural residue of pruning mulberry shoot,” *Afr. J. Biotechnol.*, vol. 9, no. 19, pp. 2762–2767, 2010.

[69] Q. Qian, M. Machida, and H. Tatsumoto, “Preparation of activated carbons from cattle-manure compost by zinc chloride activation,” *Bioresour. Technol.*, vol. 98, no. 2, pp. 353–360, 2007.

[70] R. Malik, D. S. Ramteke, and S. R. Wate, “Physico-chemical and surface characterization of adsorbent prepared from groundnut shell by ZnCl2 activation and its ability to adsorb colour,” *Indian J. Chem. Technol.*, vol. 13, no. 4, pp. 319–328, 2006.

[71] T. H. Liou, “Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation,” *Chem. Eng. J.*, vol. 158, no. 2, pp. 129–142, 2010.

[72] J. E. G. Mdoe and L. L. Mkayula, “Preparation and characterization of activated carbons from rice husk and shells of palm fruits,” *Tanzania Journal of Science*, vol. 28, no. 2. pp. 131–142, 2002.

[73] T. W. Ahmad, T. H. Usmani, and Z. Ahmad, “Activated carbon from indigenous inferior woods part ii. Activation temperature, time and particle size influence.,” *Pak. J. Sci. Ind. Res.*, 1990.

[74] S. B. Daffalla, H. Mukhtar, and M. S. Shaharun, “Properties of activated carbon prepared from rice husk with chemical activation,” *Int. J. Glob. Environ. Issues*, vol. 12, no. 2, pp. 107–129, 2012.

[75] H. Onyeka, “Preparation and Characterisation of Activated Carbon from Agrowastes Peanut Seed (African Canarium) and Palm Kernel Shell,” vol. 3, no. 13, pp. 418–441, 2014.

[76] Y. Örkün, N. Karatepe, and R. Yavuz, “Influence of temperature and impregnation ratio of H 3PO 4 on the production of activated carbon from hazelnut shell,” *Acta Phys. Pol. A*, vol. 121, no. 1, pp. 277–280, 2012.

[77] B. S. Girgis and a. N. a El-Hendawy, “Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid,” *Microporous Mesoporous Mater.*, vol. 52, no. 2, pp. 105–117, 2002.

[78] Y. Diao, W. P. Walawender, and L. T. Fan, “Activated carbons prepared from phosphoric acid activation of grain sorghum,” *Bioresour. Technol.*, vol. 81, no. 1, pp. 45–52, 2002.

[79] M. A. Ahmad, N. A. Ahmad Puad, and O. S. Bello, “Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation,” *Water Resour. Ind.*, vol. 6, pp. 18–35, 2014.

[80] F. Rodríguez-reinoso, “The role of carbon materials in heterogeneous catalysis,” *Carbon N. Y.*, vol. 36, no. 3, pp. 159–175, 1998.

[81] H. Marsh and F. R. Reinoso, *Activated carbon*. Elsevier, 2006.

[82] H. P. Boehm, “Some aspects of the surface chemistry of carbon blacks and other carbons,” *Carbon N. Y.*, vol. 32, no. 5, pp. 759–769, 1994.

[83] B. S. Girgis, E. Smith, M. M. Louis, and A. N. a El-Hendawy, “Pilot production of activated carbon from cotton stalks using H3PO4,” *J. Anal. Appl. Pyrolysis*, vol. 86, no. 1, pp. 180–184, 2009.

[84] a. N. a El-Hendawy, “Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions,” *J. Anal. Appl. Pyrolysis*, vol. 75, no. 2, pp. 159–166, 2006.

[85] M. E. Fernandez, G. V. Nunell, P. R. Bonelli, and A. L. Cukierman, “Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes,” *Ind. Crops Prod.*, vol. 62, pp. 437–445, 2014.

[86] R. E. Franklin, “Crystallite growth in graphitizing and non-graphitizing carbons,” in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 1951, vol. 209, no. 1097, pp. 196–218.

[87] T. Bohli, A. Ouederni, N. Fiol, and I. Villaescusa, “Evaluation of an activated carbon from olive stones used for heavy metal removal from aqueous phase,” vol. 18, pp. 88–99, 2015.

[88] W. Tongpoothorn, M. Sriuttha, P. Homchan, S. Chanthai, and C. Ruangviriyachai, “Preparation of activated carbon derived from Jatropha curcas fruit shell by simple thermo-chemical activation and characterization of their physico-chemical properties,” *Chem. Eng. Res. Des.*, vol. 89, no. 3, pp. 335–340, 2011.

[89] S. Salehin, A. S. Aburizaiza, and M. a. Barakat, “Activated carbon from residual oil fly ash for heavy metals removal from aqueous solution,” *Desalin. Water Treat.*, no. April 2015, pp. 1–10, 2015.

[90] O. Y. BAKATHER, “REMOVAL OF LEAD & CHROMIUM FROM WATER BY USING MODIFIED & NONMODIFIED CARBON NANOTUBES.” King Fahd University of Petroleum and Minerals, 2009.

[91] Y. H. Li, Z. Di, J. Ding, D. Wu, Z. Luan, and Y. Zhu, “Adsorption thermodynamic, kinetic and desorption studies of Pb2+ on carbon nanotubes,” *Water Res.*, vol. 39, no. 4, pp. 605–609, 2005.

[92] V. C. Taty-Costodes, H. Fauduet, C. Porte, and A. Delacroix, “Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris,” *J. Hazard. Mater.*, vol. 105, no. 1–3, pp. 121–142, 2003.

[93] A. Seco, C. Gabaldón, P. Marzal, and A. Aucejo, “Effect of pH, cation concentration and sorbent concentration on cadmium and copper removal by a granular activated carbon,” *J. Chem. Technol. Biotechnol.*, vol. 74, no. 9, pp. 911–918, 1999.

[94] M. Kobya, E. Demirbas, E. Senturk, and M. Ince, “Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone,” *Bioresour. Technol.*, vol. 96, no. 13, pp. 1518–1521, 2005.

[95] G. Vázquez, J. Gonzalez-Alvarez, S. Freire, M. López-Lorenzo, and G. Antorrena, “Removal of cadmium and mercury ions from aqueous solution by sorption on treated Pinus pinaster bark: kinetics and isotherms,” *Bioresour. Technol.*, vol. 82, no. 3, pp. 247–251, 2002.

[96] R. Ayyappan, A. C. Sophia, K. Swaminathan, and S. Sandhya, “Removal of Pb (II) from aqueous solution using carbon derived from agricultural wastes,” *Process Biochem.*, vol. 40, no. 3, pp. 1293–1299, 2005.

[97] A. S. Thajeel, M. M. Al-Faize, and a. Z. Raheem, “Adsorption of Pb+2 and Zn+2 ions from oil wells onto activated carbon produced from rice husk in batch adsorption process,” *J. Chem. Pharm. Res.*, vol. 5, no. 4, pp. 240–250, 2013.

[98] V. C. Srivastava, I. D. Mall, and I. M. Mishra, “Adsorption of toxic metal ions onto activated carbon,” *Chem. Eng. Process. Process Intensif.*, vol. 47, no. 8, pp. 1269–1280, 2008.

[99] M. M. Rao, D. K. Ramana, K. Seshaiah, M. C. Wang, and S. W. C. Chien, “Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls,” *J. Hazard. Mater.*, vol. 166, no. 2–3, pp. 1006–1013, 2009.

[100] Y. B. Onundi, a. a. Mamun, M. F. Al Khatib, and Y. M. Ahmed, “Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon,” *Int. J. Environ. Sci. Technol.*, vol. 7, no. 4, pp. 751–758, 2010.

[101] P. Senthil Kumar and R. Gayathri, “Adsorption of Pb2+ ions from aqueous solutions onto bael tree leaf powder: Isotherms, kinetics and thermodynamics study,” *J. Eng. Sci. Technol.*, vol. 4, no. 4, pp. 381–399, 2009.

[102] D. Mohan and S. Chander, “Single component and multi-component adsorption of metal ions by activated carbons,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 177, no. 2–3, pp. 183–196, 2001.

[103] Z. Aksu and T. Kutsal, “A bioseparation process for removing lead (II) ions from waste water by using C. vulgaris,” *J. Chem. Technol. Biotechnol.*, vol. 52, no. 1, pp. 109–118, 1991.

[104] D. Mohan, C. U. Pittman, M. Bricka, F. Smith, B. Yancey, J. Mohammad, P. H. Steele, M. F. Alexandre-Franco, V. Gómez-Serrano, and H. Gong, “Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production,” *J. Colloid Interface Sci.*, vol. 310, no. 1, pp. 57–73, 2007.

[105] T. Depci, A. R. Kul, and Y. Önal, “Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single- and multi-solute systems,” *Chem. Eng. J.*, vol. 200–202, pp. 224–236, 2012.

[106] F. Qin, B. Wen, X. Q. Shan, Y. N. Xie, T. Liu, S. Z. Zhang, and S. U. Khan, “Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat,” *Environ. Pollut.*, vol. 144, no. 2, pp. 669–680, 2006.

[107] D. Mohan, C. U. Pittman, and P. H. Steele, “Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin-a biosorbent,” *J. Colloid Interface Sci.*, vol. 297, no. 2, pp. 489–504, 2006.

[108] Q. Li, S. Wu, G. Liu, X. Liao, X. Deng, D. Sun, Y. Hu, and Y. Huang, “Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of Phanerochaete chrysosporium,” *Sep. Purif. Technol.*, vol. 34, no. 1–3, pp. 135–142, 2004.

[109] D. Mohan and K. P. Singh, “Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse--an agricultural waste.,” *Water Res.*, vol. 36, no. 9, pp. 2304–2318, 2002.

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